Computational Design of Inhibited Prmers

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ABSTRACT

Virtual design of materials would allow the sorting and selection of the material designs with the highest probability of fulfilling their function. This has the potential to dramatical cut the time for materials development. and thus focus material development. It requires the integration of models from the molecular to engineering scale. This paper reports on this platform and the actual models across the scales. The models include: Molecular scale models defining corrosion inhibitor/surface interactions and inhibitor movement, Models of pit initiation and propagation , microclimate models defining conditions in and on the exterior of an aircraft and damage accumulation models that keep track of the advance of damage . The system can estimate the life of a range of primers with different inhibitors for different flight patterns.

Keywords: airframes, inhibitors, primer, computational design, molecular modelling

1 INTRODUCTION

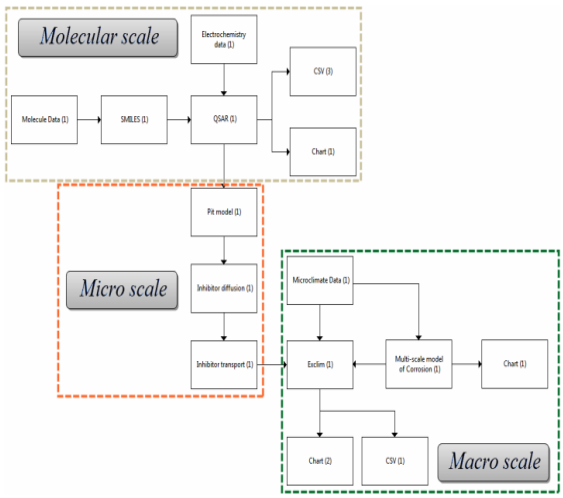
If new materials are to be used in new aircarft then it is necessary to reduce the time to develop such materials (currently up to 15 years) to less that the time to develop aircraft (currently 6-8 years) [1]. Currently new materials must be planned a generation ahead of air-platforms, and clearly specifications may change for those platforms. Materials development time may be divided into the discovery phase, the research and development phase, scale up, certification and testing and then production optimization. The use of tools such as computational design has the potential to significantly reduce the discovery and research and development phase for new materials [2]. Further , material designers and fabrications are learning how to use molecular structures to give enhanced performance of finished components. If the design space opened up by molecular design is to be used effectively we need tools that can search rapidly this expanded design space.

If computational design is to be effective for designers it needs to go past predicting basic material properties and must predict the effect of changes in the structure and design of materials on the life of full scale components in service. In this paper the application of computational design to predict the effective service life of primers on aluminium containing green inhibitors will be presented. Traditionally chromates (particularly strontium chromate) have been added to primers to provide ongoing active inhibition against metal corrosion [3]. These chromate will leach out of the primer and migrate to any exposed metal surfaces (bottom of cracks) where it can bind to the surface reducing the probability of corrosion. Unfortunately chromate is a human toxin and is being withdrawn from service so new safe inhibitors are required [4]. Two significant groups are of interests, the rare earths [5] (cerium, lanthanum, praseodymium) and organic heterocyclic structures [6]. The heterocyclic compounds can be effective anodic inhibitions while their efficiency depends critically on what functional groups are attached to the ring structures, where on the ring the groups are attached [6], and how electrons are redistributed once the molecule has absorbed onto a surface. The rare earth elements can act as cathodic inhibitors, by promoting the development of mixed oxides on cathodic sites. Thus, the effectiveness of inhibitors in coatings will depend on the ability of the inhibitor to bond to the surface (which is controlled by its molecular structure in the case of organic inhibitors) and the ability of the coating system to deliver a sufficient concentration of inhibitor to defects in its structure. Of course to calculate the total life of a paint film the environments that the aircraft fly through and in particular humidity and temperature, surface wetness and pollutant deposition needs to considered which requires a detailed knowledge of conditions along an aircrafts flight path. Thus a multi-scale model to permit the design of inhibited paint films would have to span scales from 10^{-10}m to 10^{6}m. At present a range of multi-scale corrosion models have been developed [7] and while some cover an impressive range of scales [8] from around 10^{-6}m to 10^{6}m this range must be extended to permit computational design. Computational design will provide reasonable estimate of the probable effective life of material systems. This is critical for the development of new coatings for while the industry has over 50 years experience of strontium chromate there is no equivalent knowledge for the new coatings

Thus this paper will outline the development of computational design and multi-scale modelling of inhibited coatings applied to airframes. It will highlight the advantages of building an adaptable system based on a flexible platform that can integrate models, data and information across a range of scales. It will explore the lessons learned in developing such a system and highlight limitations and challenges to be addressed

2 MULTI-SCALE FRAMEWORK

A system framework has been designed to link together models across the scales from 10^{-10}m to 10^{6}m in a dynamic manner via the hierarchal linking/interconnection of these modules. The model framework also permits incorporation of experimental data and subsequent modification of such data and upgrading of models (e.g quantative structure activity relationship (QSAR) models) partially based on this data. Figure 1 shows a work flow diagram of the multi-scale model. Each box represents a separate computer model. The modules occur across three levels, molecular , micron and macro scale . Individual modules can be replaced and connected to a range of other modules. Broadly the molecular modules calculate how the molecular structure of the inhibitor controls there ability to regulate electrochemical processes, the micron modules calculate the transport of inhibitors to defects in a paint film and the growth of pits at such defects while the macro models calculate the micro climate within and on the exterior of an aircraft as a function of aircraft usage and the development of total damage at defects . Unfortunately given the length of this paper it is not possible to outline all the modules so to give a "flavor" of the system the molecular scale modeling with be outlined.



. Figure 1. Multi-Scale Model Structure

3 MOLECULAR TO ELECTROCHEMICAL SCALES

To calculate molecular properties which may be relevant to corrosion inhibition efficacy, density functional theory (DFT) was employed. A module which links a supercomputer hosted version of SIESTA [9] (a DFT code) to the multi-scale design framework has been created. The module calculates inhibitor's molecular structure and properties (electron affinity, ionization potential, fundamental bandgap, Mulliken electronegativity, chemical hardness and chemical potential) of the investigated corrosion inhibitor molecule. The specifics of the SIESTA calculations are as follows: the exchange correlation functional of Perdew-Burke-Ernzerhof within the generalized gradient approximation (GGA) with a cut off energy of 500 Ry employed throughout. A double zeta plus polarization (DZP) basis set was used for all calculations, and norm-conserving pseudopotentials were used as supplied with the SIESTA code without further modification. Geometry optimisation was performed with the conjugate gradient (CG) algorithm until the residual forces on atoms were less than 0.01 eV/Å, and the difference in total energy between SCF steps was less than 10^{-4} eV. Potential corrosion inhibitor molecules were modeled by centering a molecule into a fixed 30 $Å^3$ supercell using the Γ-point only, and allowing full structural relaxation.

In addition to molecular properties generated from DFT calculations, other properties or descriptors (e.g. number of sulfur atoms, number of ionized sulfur atoms, number of ionized COOH groups, number of rings, number of hetero-aromatic nitrogen groups, total molecular charge) are derived using the DRAGON program[10]. All the molecular properties and descriptors are then combined with experimental data on inhibitor performance and run through a quantitative structure property relationship (QSPR) module[11, 12]. Experimental data can take various forms such as measured inhibitor efficiency or particular electrochemical parameters. The QSAR module uses machine learning methods to build relationships between molecular properties and experimental values related to corrosion electrochemical properties from molecular properties and descriptors.. The performance of the models was assessed and is presented in Figure 2.

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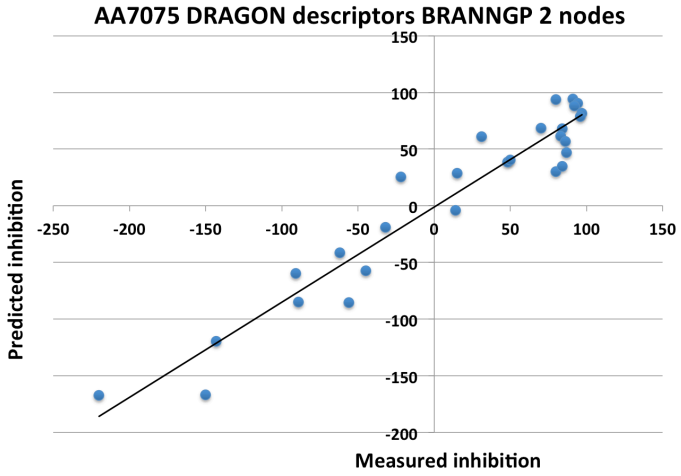

Figure 2. The observed versus predicted corrosion inhibition for 7075 alloy. panel shows models for entire data set of 28 compounds.

4. CORROSION AND MACROSCALES

Corrosion can occur if the surface is wet and two modules have been developed to predict when such moisture will occur on surfaces: one module is applied to the exterior of a plan and the other to the interior. In both models the user defines a usage pattern of the aircraft, which provides flight schedules and particulars concerning flight patterns, speeds, storage on ground etc. The exterior approach uses processes models [13] and meteorological data to estimate likely moisture events based on past meteorological information for flight locations, as exterior relative humidity is very low above the cloud level formation of wetness layers on surfaces in flights will not occur and so wetness events need only be calculated when the aircraft is on ground although pollutants may deposit in flight [14]. Models include analytical models of aerosol formation and computer fluid dynamic models of aerosol transport and deposition onto aircraft [14], analytical and heat and mass transfer models for prediction surface temperatures and evaporation and condensation [15] and computer fluid dynamics and analytical models for predicting drop movement on a surface and retention of contaminates on a surface[16]. The approach for predicting wetness on surfaces within an airframe is quite different [17]. Wetness events on surfaces within an aircraft will often occur because of human intervention, either directly (spilling a drink, etc.) or indirectly (failure to replace an insulation blanket that leads to condensation) so that it is difficult if not impossible to predict such events from process models [18].

Rather semi-empirical models are developed from direct measurements of wetness and microclimate on aircraft in flight. Two cases are identified, where wetness events are explicable in terms of standard thermodynamics of moist air (condensation, evaporation) and where they are not and appear associated with human activity (spills in the galley or lavatory etc). In the later case a probabilistic model of the occurrence of moisture is developed directly from direct measurement of the frequency of human induced moisture events. In the former case the microclimate data is used to develop two empirical models, one of the rate of air exchange between the interior environment of the sub-floor and the air exterior to the aircraft and the other of the rate of change in temperature of surfaces in the subfloor of an aircraft after landing. These two models are combined with meteorological data defining air conditions on ground and in flight to predict the probability of condensation and evaporation as the aircraft flies between bases around the globe [19].

5. DISCUSSION

The paper indicates that by linking models together it may be possible to predict the life of an inhibited primer in service. If proven this will be an important conclusion as it will allow virtual design of real structures in real service conditions. This would allow permit the many design options opened up by our increasing control of molecular structure to be investigated while reducing the time required for new materials development. The corollary of this conclusion is that the demand on scientist's time to construct such a series of linked model is very high. One way to reduce this time is to make use of existing models and existing data and to access such information from a range of institutions and researchers and to have a range of research groups collaboratively developing new models. An open framework and flexible framework is required if this approach is to be adopted. The model system outlined combines a number of sources and types of information, information from experimental and monitoring programs, information extracted from on-line data sources and tools and information calculated from in-house programs. It is very unlikely that a system of in-house models will be able cover the scales required, not just because of man hours required, but because the theoretical frameworks connecting different models (e.g. molecular and electrochemical) are not sufficiently established, or in the case of aircraft microclimate the variability and uncertainty in parameters is too high. In these cases approaches based on data (such as the use of QSAR to connect molecular properties and electrochemical parameters) are required. However data based approaches also offer the advantage that as the data is enriched, defined relationships between outputs and inputs can be refined so the framework can develop.

5 CONCLUSIONS

The paper has outlined how computational design of inhibited primers is possible if based on a multi-scale and

flexible framework . Further it is evident that purely analytical models are unlikely to cover and link the multi-scales for the foreseeable future and thus the inclusion of data and data derived models will be necessary for the foreseeable future due to conceptual and theoretical gaps between scales and processes. However such data derived approaches also offer the possibility of adapting the approach when additional data is available.

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