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Computational design and optimization of multilayered and functionally graded corrosion coatings

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ABSTRACT

This paper describes a computational approach to analysis and optimization of compositionally graded coatings for cathodic protection. Time-dependent galvanic corrosion is simulated by coupling a finite element electrochemical model with calculated rates of metal dissolution. A simulated annealing optimization algorithm is applied to the time-dependent corrosion model to determine coating structures that maximize desired protective qualities. This computational approach to coating design is applied to a hypothetical graded zinc-alloy coating with a circular defect on an iron substrate, in an aerated NaCl electrolyte. A linear compositional gradient increases the predicted duration of cathodic protection by 84% over an equivalent monolithic coating, while the optimized coating structure further improves protection time to a total increase of 112%. The optimized coating structure consists of a thin barrier layer adjacent to the substrate, with a thicker sacrificial layer on the exterior and a short region of graded composition in between. The overall approach to optimization of coating structure is shown to be robust, efficient, and produce non-obvious designs with significant improvement in coating performance, and thus has potential to be of significant utility in practical corrosion coating design.

1. Introduction

In recent years there have been a number of parallel developments in adjacent science and engineering spaces, which could open the door to a new generation of "smart" corrosion coatings. These include (i) improved corrosion simulation methodologies, (ii) wide dissemination of optimization algorithms for engineering design, and (iii) new coating technologies that can modulate and grade the structure and chemistry of a coating. Consider each of these in turn.

First, the rise in computational power has dramatically improved the predictive ability of numerical corrosion models for complex systems such as a galvanically-coupled coating-substrate pair. Whereas early analytical work on galvanic coating systems required very simplified conditions (simple geometry and active dissolution in acidic electrolytes) to achieve close agreement between calculated potential distributions and experimental measurements [1,2], more recent models can address more complexities such as non-acidic environments, longer timescales, and also non-steady state phenomena. For instance, at the cut edge of galvanized steel in neutral aerated NaCl solution, formation of a zinc-based oxide film has been shown to inhibit the cathodic O_2 reduction reaction on the steel surface [3–5]. This effect was modeled by Thébault et al. by incorporating a region of complete cathodic inhibition on the steel surface adjacent to the zinc, reporting good agreement between calculations and in-situ current density measurements taken via the scanning vibrating electrode technique [4,5]. Likewise, a pair of computational studies by Brown and Barnard [6,7] looking at corrosion at the cut edge of steel with a 4.5 wt.% Al zinc-based coating showed that the increased corrosion resistance associated experimentally with finer coating microstructure [8] could be explained by inhibition of O_2 mass transport through precipitated corrosion product layers. Deshpande [9,10] modeled a galvanic couple between mild steel and magnesium alloy AE44 in NaCl solution, incorporating time dependent changes in surface contours due to predicted metal dissolution. Good agreement between the model and surface profile measurements was reported, at least for a 3 day immersion period. Although many mechanisms underlying corrosion are not fully understood, such as corrosion product film formation and diffusion through it, it is clear that computational studies are able to qualitatively capture the behavior of corroding systems under reasonable conditions. Taken as a whole, the recent progress in computational modeling of corrosion portends a future where modeling need not only be used to analyze known corrosion situations, but potentially to predict and engineer corrosion coatings with improved performance.

Second, the many engineering disciplines that rely on design methodologies have recently spawned a variety of facile and versatile optimization algorithms and routines. In particular, the

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development of stochastic optimization techniques such as simulated annealing (SA), has allowed robust optimization of functions with many local extrema, or over discrete domains, for which traditional gradient-based optimization methods cannot be effectively applied. The SA class of algorithms, first described by Kirkpatrick et al. [11] and by Černý [12], work by analogy with the physical annealing process, with the value of the objective function corresponding to an effective "energy" of the system. Steps that increase the total "energy" are accepted with a finite probability, allowing escape from local minima. SA techniques have been successfully applied to a number of practical optimization problems in engineering, such as design of efficient acoustic filters [13], low cost truss structures [14], and many others [14–17]. Due to its flexibility, SA has several advantages over traditional gradient-based techniques for optimization of engineering designs, as it can be easily applied to complex or non-continuous search spaces, and it does not require the calculation of gradients. Thus SA is often the technique of choice when optimizing the output of a coupled FE model [15,16,18], as gradients cannot be calculated due to the approximate nature of the outputs. While this approach, to our knowledge, has not yet been applied to corrosion problems or coatings, when coupled with a computational model of corrosion, the SA technique is well suited to optimization of coating structures.

Third, coatings technologies have advanced to the point where, at scale, complex alloy coatings with designed internal structures are possible. For example, vacuum processes such as physical vapor deposition, or sputtering with multiple targets or controlled gas input can produce compact, adhesive coatings with layers of precisely controlled composition [19–21]. Electrodeposition technologies allow control or modulation of chemistry, grain size, or both, via complex dual-bath techniques or a variety of more scalable single bath techniques [22–26]. Recent studies have also reported low cost synthesis of composite coatings by electrodeposition of a base layer prior to hot dip galvanizing [27,28]. Many such coatings have been produced and tested in a variety of corrosion conditions, and in some cases it has been shown that coatings with a graded composition are significantly more protective than monolithic coatings of equal thickness. For example, superior corrosion resistance of electrodeposited coatings with multilayer structures or composition gradients has been reported for Zn/Co [29], Zn/Ni [30], Zn/Zn–Mn [31], and Zn–Fe/Ni [32,33] coatings synthesized via dual bath techniques, and Zn–Ni [34–37], Zn–Fe [38], and Zn–Co [29] coatings synthesized via single bath techniques. Fei and Wilcox [30] found increased time to red rust formation in a neutral salt spray test for Zn/Ni coatings relative to monolithic Zn or Ni coatings of equivalent thickness, which they attributed to synergism between barrier protection due to the Ni layers and sacrificial protection due to the Zn layers. Rahsepar and Bahrololoom [32,33] likewise found improved salt spray test performance for Zn–Fe/Ni coatings, and reported that the multilayer coatings exhibited finer microstructure, decreased surface roughness, and a more compact and protective oxide film. Sa-nguanmoo et al. [28] showed that electrodeposition of a Ni layer on steel prior to hot dip galvanizing improved the uniformity and adhesiveness of the zinc coating, and decreased rust formation after 1400 h of salt fog exposure. At present, from a global perspective these various studies must be viewed as a scattered assemblage of isolated data points. Nonetheless, it is clear that processing technology is capable of producing non-monolithic coatings with complex internal structures, and that there is great untapped potential for improvements in corrosion resistance.

The three parallel developments described above together comprise a recipe for rapid progress in corrosion coating development: combining advances in (i) computational corrosion modeling and (ii) optimization techniques could lead to a rapid computational search for preferred coatings with compositional gradients, multilayer structures, etc. With (iii) advanced coating technologies able to produce such optimized structures, a full path from design to deployment can be envisioned. It is our belief that such an integrated computational approach may in fact be necessary to the successful development of advanced graded or multilayer coating structures, simply because these structures have a very large number of degrees of freedom, both in terms of processing technique, and the number, thickness, and composition of the layers; performing an experimental search for preferred multilayered or graded corrosion coatings would not only be slow and costly, but it may never identify truly optimized structures. And, given the diversity of corrosion media and conditions for which coatings may be employed, this empirical exploration would need to be conducted in parallel many times to address each situation individually. Small differences in the coating design can also have large impact on the corrosion performance. For example, while a 12 μm coating of electrodeposited 2 μm Zn/Ni layers exhibit improved protection of a steel substrate relative to a 12 μm Zn coating, similar coatings with 1 μm layers or with the order of exactly the same sequence of layers reversed, exhibit decreased protection time in salt spray tests [30]. The iterative design process is also compounded by the difficulty of experimentally predicting corrosion resistance from laboratory tests. Common electrochemical tests, such as potentiodynamic polarization or electrochemical impedance spectroscopy, provide aggregate information about surface reactivity but neglect localized effects and ignore the contribution of layers not yet exposed to the surface. Accelerated corrosion tests, such as the salt spray test or cyclic wet–dry tests, empirically measure corrosion resistance but may not accurately reflect behavior in field conditions, and generally have long cycle times for iterative design purposes.

We perceive that there is therefore great potential applicability for a computational tool that would allow simulation and optimization of the corrosion protection afforded by multilayered or graded coating structures, which could be used to speed up the design cycle. Our goal in the present paper is to present the first steps towards this goal, by demonstrating how the introduction of optimization methods to corrosion modeling can quickly yield predictions for preferred coating structures. While the specific problem studied here is intentionally simple – galvanic corrosion near a scar in a coated component – the results strongly support greater use of optimization in the design of "smart" corrosion coatings with improved performance.

2. Corrosion simulations

As noted in Section 1, our approach requires the integration of (i) simulations of corrosion for a coating/substrate pair, with (ii) optimization algorithms to evolve the structure and identify preferred coating structures. In the following we introduce these two components separately; the purpose of the present section is to address (i). Our goal here is not to advance the state of the art in corrosion modeling, per se, but to build a simple, illustrative model that we can integrate with the optimization component in a later section.

2.1. Geometry

We select for our demonstration system a substrate coated with a sacrificial (galvanic) coating. We envision a multilayer coating in which each layer is more active than the one beneath it, and all layers are expected to undergo active dissolution in the electrolyte. The basic geometry of the system is selected to capture the effect of localized galvanic protection near a scar in the coating which