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Validated numerical modeling of galvanic corrosion of zinc and aluminum coatings

Samuel R. Cross, Srikant Gollapudi, Christopher A. Schuh *

Department of Materials Science and Engineering, MIT, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

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ABSTRACT

A time-dependent finite element model was developed to simulate the corrosion of zinc and aluminum coatings, galvanically coupled to a mild steel substrate in deaerated 0.01 M H_2SO_4 electrolyte. The simulations of galvanic corrosion for each of the coatings were compared to experimental measurements of open circuit potential, and changes in coating geometry measured via surface profilometry. Good agreement between the model predictions and corrosion tests were observed initially for both coatings. However, in the case of the zinc coating, divergence was observed between the simulation and the corrosion test after approximately 40 min, due to a decrease in the reactivity of the zinc surface.

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1. Introduction

Galvanic corrosion occurs due to electrochemical coupling between two metals with different corrosion potentials in a common electrolyte, leading to a decreased corrosion rate for the more noble metal and an increased corrosion of the more active one. This is desirable in many engineering applications, a prime example being galvanized steels, where the galvanic coupling protects any steel exposed due to pores or defects in the coating [1]. However, the excess cathodic currents on any exposed steel increase the dissolution rate of the nearby coating, resulting in decreased service life of the coating. Thus there is significant value in studying the process of galvanic corrosion, in order to predict the throwing power of the coating and its service lifetime [2]. This will aid in design of coatings for optimally effective sacrificial protection that minimizes coating loss.

In recent years, there has been great progress in computational modeling of galvanic corrosion by solving field-based equations for the distribution of potential and dissolved chemical species in the electrolyte [3–20]. During galvanic corrosion, the more noble metal supports net cathodic current, while the more active metal supports net anodic current. This separation of interfacial current is balanced by ionic currents in the electrolyte, carried by motion of dissolved charged species due to potential and concentration gradients. The resulting distribution of potential in the electrolyte can be calculated by solving coupled partial differential equations through numerical integration, most commonly the finite element method [4,7–20]. This modeling approach has been quite successful at capturing many aspects of the behavior of corroding systems, particularly for short times and acidic electrolytes, in which complicating factors such as corrosion product precipitation, surface oxide formation, and changes of geometry due to metal dissolution are less prominent. For instance, good agreement has been demonstrated between numerical models and current density measurements of corroding Zn/Cu [3] and Fe/Cu [4] couples in acidic electrolytes, and Zn/steel [7,9] and Mg/steel [12] couples in neutral NaCl electrolytes. More recent studies have also tracked concentrations of dissolved chemical species in the electrolyte, by solving coupled equations for diffusion and electromigration [7,8,14,17–20], allowing prediction of a wide range of concentration effects. While such models have not been extensively validated, they have been successful at capturing a number of corrosion phenomena, such as regions of zinc hydroxide precipitation in galvanized steel immersed in NaCl solution [8], and pH profiles along a corrosion crevice in 304 stainless steel [14,21].

As calculated distributions of potential allow prediction of instantaneous metal dissolution rates, time-dependent simulations of galvanic corrosion can be generated through a variety of moving boundary techniques [5,6,10,11,13–15,18,19], which account for the changes in the geometry of the system over time. Brown and Barnard used a time-dependent model to simulate corrosion of a Zn–5 wt.% Al coatings coupled to a steel substrate [5,6], showing that refinement of coating microstructure decreases zinc loss over time, in agreement with experimentally observed trends, but not directly comparable to the experiments in a quantitative sense [22]. Deshpande [10,11] used a time-dependent model with moving boundaries to simulate galvanic corrosion of coplanar magne-

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* Corresponding author.
E-mail address: schuh@mit.edu (C.A. Schuh).

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sium alloy AE44-steel and AE44-aluminum alloy couples in neutral NaCl solution. He compared the model results with current density measurements taken using the scanning vibrating electrode technique, and surface profiles taken following a three day immersion test. Good agreement was reported between predicted and measured current densities, and surface profiles were found to match well for the AE44-mild steel, but the model underestimated the corrosion rate in the AE44-aluminum alloy couple. In our recent work, we proposed that time-dependent galvanic corrosion modeling could be combined with optimization algorithms, to design preferred coating architectures with, e.g., functional gradients in corrosion potential built into them [15]. That work was however only computational, and experiments on multilayered or functionally graded coated in general have not been compared with any predictive simulation.

Despite the widespread deployment and significant commercial value of galvanic coatings, in particular zinc-based coatings, for protection of steel, to our knowledge there have not been any attempts to directly compare experimental measurements of corrosion of galvanic coatings to time-dependent models. Such validation is critically important to confidently use computational modeling as a tool for prediction of coating performance and design of coatings with improved properties. Thus, in the present study, the accuracy of time-dependent simulations of the galvanic corrosion of zinc and aluminum coatings over steel substrates is investigated, through direct comparison of model outputs and experimental measurements.

2. Experimental

2.1. Synthesis of coatings

Coatings were deposited on mild steel substrates using electron beam deposition. Steel specimens 20 × 10 × 1 mm in size were ground sequentially with 240, 600, 1200, 2400, and 4000 grit emery papers. Subsequently the specimens were polished with 6, 3 and 1 μm diamond suspensions to achieve a mirror finish, ultrasonicated in ethanol for 2 min and etched for 5–10 s with mild hydrochloric acid. The specimens were again cleaned with ethanol and dried before being plasma cleaned for a period of 3 min. The plasma was generated in an oxygen atmosphere at a pressure of 0.5 torr and 200 W power. The specimens used for corrosion tests were masked with a thin strip of steel, 20 × 1.5 × 0.5 mm, held in tight contact with the steel substrate by clamps, and placed across the sample surface so as to divide it into two equal halves. The specimens were loaded into an electron beam deposition chamber (Varian 904/Sloan Pak-8). The chamber was initially purged with nitrogen and then pumped down with a roughing pump followed by a diffusion pump to a vacuum of approximately 10^{-6} torr. Deposition was carried out at a voltage of 8 kV and a current of 0.25 A and 0.02 A for aluminum and zinc, respectively. The deposition rate was maintained at 3–4 Å/s for aluminum and 2–3 Å/s for zinc. Following deposition, the specimens were allowed to cool inside the chamber under vacuum conditions for approximately 45 min. Subsequently they were removed from the chamber and the masks were unclamped. The resulting geometry was a coating over the sample surface except for an exposed strip down the center of the specimen, as shown in Fig. 1a. In order to improve adhesion, the zinc coatings were heat treated at 300 °C for 15 min in an argon atmosphere. The coated steel specimens were then characterized through profilometry, scanning electron microscopy and corrosion tests.

2.2. Polarization curves

Polarization curves were measured for a bare steel substrate as well as zinc and aluminum deposited on glass so as to remove any possible contribution from the substrate. The samples were masked to expose a 1 × 1 cm area, and immersed in 10 mM H_2SO_4 electrolyte solution in a Gamry multiport corrosion cell. The solution was deaerated by purging with nitrogen gas for 2 h.

The polarization curves were captured at a scan rate of 0.5 mV/s in the anodic direction, using a PARSTAT 2273 potentiostat (Princeton Applied Research). The potential was measured using a silver/silver chloride reference electrode (Gamry), coupled to the electrolyte through a fritted capillary tube with its tip placed adjacent to the sample. For the aluminum and zinc samples, the potential was swept from −200 mV to +200 mV relative to the initial open circuit potential. For the steel sample, the potential was swept from −400 mV to +250 mV relative to the open circuit potential. Measurements for the steel substrate and aluminum on glass were taken following 30 min of immersion in the electrolyte. However in the case of the zinc coating, due to its high rate of dissolution, measurements were taken immediately following immersion in acid.

2.3. Corrosion testing

Corrosion tests were performed on steel with zinc and aluminum coatings, deposited on the samples partially masked as described above, to expose a strip of substrate of approximate width 1.5 mm after deposition (Fig. 1a). For corrosion testing the samples were masked to expose a 1 × 1 cm area, bisected by the strip of exposed substrate. The coated samples were immersed in deaerated 10 mM H_2SO_4, and the open circuit potential measured throughout the period of immersion. The tests were interrupted and the samples removed periodically for profilometry measurements using a KLA Tencor P-16 surface profilometer. Immediately after removing the coated samples from the electrolyte, they were immersed in ethanol to wash away the electrolyte and dried thoroughly with compressed air. They were scanned with the profilometer stylus at a rate of 50 μm/s under a load of 20 mg, with a range and resolution of 131 μm and 0.0781 Å respectively. In order to minimize potential atmospheric corrosion of the coated samples, the profilometry measurements were taken within 10 min of removal from the electrolyte. For each sample, scans were taken at three different locations to check for repeatability of data. The data were slope-corrected for better visualization and quantitative comparisons.

3. Model

3.1. Model system

Corrosion simulations were performed on a geometry modeling a 1 cm wide strip of coated steel, with a half centimeter insulating surface on either side, i.e. a geometry designed to match that of the experimental system as shown in Fig. 1a. The coatings were taken to be either pure zinc or pure aluminum, and the initial coating geometry for each simulation was taken to match the profilometry measurements of the associated coating as closely as possible, including the central masked region.

The electrolyte was modeled as a 1 cm thick layer of deaerated 10 mM H_2SO_4 electrolyte solution. Due to symmetry, modeling was performed on the right half of the electrolyte domain only, represented schematically in Fig. 1b. The geometry was discretized into 10,000 cells in the x direction, spanning the range from the center of the strip to the coating/insulator interface, so that each cell spanned a lateral distance of 0.5 μm. At a given time t, the height of the system at each of the cells was stored in a height vector $h(x, t)$, which was used to determine which metal was exposed to the electrolyte; $h > 0$ corresponds to coating being present over

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