Peridynamic modeling of pitting corrosion damage

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Ziguang Chen, Florin Bobaru *

Mechanical and Materials Engineering, University of Nebraska–Lincoln, Lincoln, NE 68588, United States

ABSTRACT

In this paper we introduce a peridynamic model for the evolution of damage from pitting corrosion capable of capturing subsurface damage. We model the anodic reaction in corrosion processes (in which electroplating is negligible) as an effective peridynamic diffusion process in the electrolyte/solid system coupled with a phase-change mechanism that allows for autonomous evolution of the moving interface. In order to simulate creation of subsurface damage, we introduce a corrosion damage model based on a sto-chastic relationship that connects the concentration in the metal to the damage of peri-dynamic mechanical-bonds that are superposed onto diffusion-bonds. We study con-vergence of this formulation for diffusion-dominated stage. The model leads to formation of a subsurface damage layer, seen in experiments. We validate results against experi-ments on pit growth rate and polarization data for pitting corrosion. We extend the 1D model to the 2D and 3D, and introduce a new damage-dependent corrosion model to account for broken mechanical bonds that enhance the corrosion rate. This coupled model can predict the pit shape and damage profile in materials with microstructural hetero-geneities, such as defects, interfaces, inclusions, and grain boundaries.

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1. Introduction

Corrosion is an extremely widespread danger to the durability and safety of structures, and there is considerable interest in this phenomenon, reflected in a large number of studies e.g. (Frankel, 1998; Ernst and Newman, 2002a, 2002b; Hunkeler and Bohni, 1981; Pistorius and Burstein, 1992). Pitting corrosion can lead to accelerated failure of structural components by perforation, or by acting as initiation sites for cracking (Frankel, 1998). Fundamental studies on pitting corrosion have focused on one of the following stages of the pitting corrosion process (Engelhardt and Macdonald, 2004; Engelhardt et al., 1997; Gaudet et al., 1986; Laycock et al., 2005; Sharland, 1987): characteristics of the passive film, the earliest stages of passive film breakdown, and the pit growth. In the present work, we mainly focus on modeling the anodic reaction involved in corrosion without considering the passive film breakdown (which we assume already broken, see Frankel (1998) for a discussion on the breakdown of passive film) or explicitly considering the repassivation. In the future we will include such mechanisms involved in pitting corrosion.

The study of pit growth is the main focus in the community of corrosion modeling. Existing models are usually of deterministic nature, aiming at describing the propagation process of an individual corrosion site. They are typically based on diffusion laws and on electrochemical kinetics laws, and deliver the geometrical evolution of the pit and the con-centration of dissolved ions throughout the corrosion site (Engelhardt and Macdonald, 2004; Engelhardt et al., 1997; Gaudet

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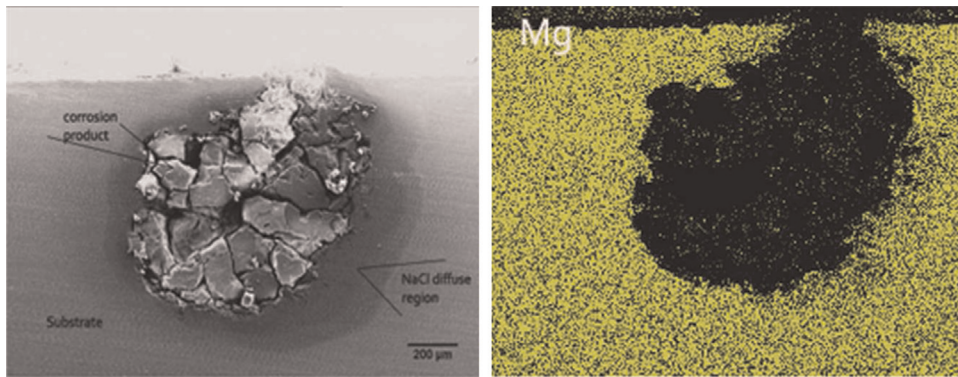
Fig. 1. Left: SEM of the cross section of a corrosion pit on a Mg-alloy sample exposed to the immersion corrosion environment after 60 h, the wetted layer is hundreds of microns thick. Right: X-ray mapping of the distribution of Mg after corrosion shows diffuse damage near the pit surface (reprinted from Song et al. (2014)).

et al., 1986; Laycock et al., 2005; Sharland, 1987). The movement of the electrode boundary was not included in the modeling of the dissolution process. More recently, Cellular Automata (CA) techniques have been introduced for the corrosion modeling (Malki and Baroux, 2005). CA models of corrosion have been improved to capture the roughening of the reaction front (Stafiej et al., 2013). In addition to CA, finite volume model has also been used to capture the diffusion and activation-controlled pitting corrosion (Scheiner and Hellmich, 2009, 2007). Most of these deterministic models are based on the diffusion in the solution, and the reaction is considered to only happen on the reaction front (the solid/liquid interface) (Engelhardt et al., 1997). Such models have successfully predicted the corrosion rate and some have been able to capture the roughening of the corrosion surface. However, since these models consider that the corrosion reaction only affects the metal surface, they cannot capture changes in the mechanical properties in the subsurface layer immediately below the solid/liquid interface. These changes, such as embrittlement induced by the corrosion or stress-dependence of the diffusion processes in corrosion, are determining factors in explaining how Stress Corrosion Cracking (SCC) is triggered and how it progresses in time (Winzer et al., 2005).

As evidenced by recent experiments, corrosion affects a subsurface region below the liquid/solid interface (Contreras et al., 2012; Song et al., 2014; Vasudevan, 2013). For example, while there are no obvious surface changes due to corrosion, a steel structure can become brittle and fail catastrophically, without going through the safer, necking deformation phase (Contreras et al., 2012). Such a phenomenon is due to embrittlement/toughness reduction induced by corrosion in a certain layer near the material surface. The reasons behind this effect are not fully understood at the moment. However, based on the SEM results and the energy dispersive X-ray spectroscopy (EDS) mapping (see Fig. 1) from Song et al. (2014), it is reasonable to assume that a layer of a certain thickness near the surface participates in the corrosion reaction. Experiments (Song et al., 2014) show that that the solution "wets" a subsurface metal layer of the corrosion pit. It is then reasonable to assume that the corrosion reaction does take place in this wetted layer. Metal ions may diffuse out from this region into the solution. This can be concluded from the X-ray maps of the cross section of a corrosion pit (Song et al., 2014), which indicates a gradient in the metal concentration, meaning that metal diffuses out from this layer near the pit surface (see Fig. 1, right panel). The reaction rate in the corrosion layer is controlled by the ionic flux. Hence, the corrosion reaction (anodic reaction) can be expressed as an effective diffusion process, in which the metal ions diffusing out into the solution and the diffusion flux (equivalent to the current density) depends on the overpotential. We assume that this dependency is similar with the one between the current density and the overpotential. We call this diffusion process, to avoid confusion, an *effective diffusion*. This idea constitutes the basis for the new model of corrosion damage we introduce in this paper.

One possible mechanism for out-diffusion of metal ions is that the solution diffused in the metal provides pathways for the metal ions to out-diffuse. The SEM results (see Fig. 1 left) in Song et al. (2014) show a region of solution diffusion inside the metal and, over the same region, a reduction in metal content (see Fig. 1 right). This reveals that corrosion does not happen on a mathematically sharp metal–solution interface, but in a layer of a finite thickness possibly reaching microns to perhaps hundreds of microns in materials with microstructures (grain boundaries, etc.). Another possible mechanism is the substitutional vacancy diffusion (see Porter and Easterling (1992)) in which the vacancy diffuse into metal from the interface, while the metal atoms are moving out. Although the vacancy diffusion coefficients in metals are very small (for example, 3×10^{-9} $\mu m^2/s$ in α-Fe at 500 °C (Callister and Rethwisch, 2007)) compared to the ionic diffusion in solution (around 10^4 $\mu m^2/s$ (Engelhardt et al., 1997; Jacobs and Wozadlo, 1988)), they can be larger by many orders of magnitude when the substitutional vacancy path is along defects such as dislocations and grain boundaries (see Porter and Easterling (1992)). For example, the grain boundary substitutional diffusion coefficient of Ga in AL-bicrystal is 10^{16} higher than that for the bulk of the crystal (Vasudevan, 2013). The combination of these two mechanisms is expected to result in corrosion reaction taking place hundreds of microns under what could be considered as the "pit surface". To our knowledge, no models of corrosion take this subsurface process into account. In modeling corrosion damage, the details of how damage evolves below the pit surface is critical for predicting where cracks will start from, especially in polycrystalline materials