Corrosion Science 82 (2014) 290–296

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Modeling dissolution controlled release of inhibitor from a damaged coating

Z. Tabor [a,*], P. Warszyński [b]

[a] Cracow University of Technology, ul. Warszawska 24, Krakow, Poland
[b] Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, ul. Niezapominajek 8, Krakow, Poland

ARTICLE INFO

Article history:
Received 21 November 2013
Accepted 23 January 2014
Available online 1 February 2014

Keywords:
C. Neutral inhibition
C. Polymer coatings

ABSTRACT

A theoretical model is proposed to explain the diversity of time profiles of the release of inhibitor to a scratch in a damaged protective coating. The model involves diffusion of an inhibitor and inhibitor release-triggering species and dissolution of inhibitor. The total mass M_I of inhibitor released to a scratch was approximated with a power function of time t: $M_I \sim t^{\alpha}$. The numerical simulations showed that, through variations in the properties of either the matrix or the inhibitor, primarily dissolution rate, α could be tuned to any value in the range from 0.5 to 1.5.

1. Introduction

Corrosion, the process that decreases the service life of plastic and metallic structures, is a worldwide problem that entails high costs related to the protection of new structures and the repair of corroded ones. The most common and cost-effective method of improving the corrosion resistance and durability of metallic and plastic structures is the application of organic coatings. In general, protection against corrosion can be accomplished in two ways: passive protection results from high adhesion of a coating to a protected surface and the creation of a barrier against corrosive species, whereas active protection can be achieved, for example, through modification of a coating with carriers of corrosion inhibitors [1]. Corrosion inhibitors can be added directly to a coating [2,3] but in some cases it can lead to degradation of coating structure [4]. To increase self-healing ability of coatings, the corrosion inhibitors can be encapsulated and the capsules are introduced into the matrix of the coating [5–8].

The release of corrosion inhibitor is triggered when a protected substrate is exposed to a corrosive environment after the coating has been damaged. The ingress of water or other species through scratches in the damaged coating results in the release of the inhibitor to an organic matrix [9]. The released inhibitor subsequently diffuses into the scratch and attaches to the exposed surface. The rate of inhibitor release into an organic matrix depends on numerous factors, including the temperature, the solubility, the pH and the properties of the coating [10–13]. It is typically assumed that the total mass M_I of inhibitor released to a scratch is proportional to a power function of time t, i.e.: $M_I \sim t^{\alpha}$, where α is the release exponent. For a special case of $\alpha = 0.5$, the release rate is Fickian, that is, the dynamics of a system is determined primarily by Fickian diffusion. If $a \neq 0.5$, then the release rate is non-Fickian (pseudo-Fickian for $\alpha < 0.5$, anomalous for $0.5 < \alpha < 1$ and superdiffusion for $\alpha \geqslant 1$ [14]). The origin of non-Fickian release rates can be qualitatively derived from anomalous diffusion in porous polymeric matrix, the specificity of interactions between inhibitor particles and various functional groups in the polymeric matrix and other particles present in the coating.

The rate of inhibitor release into a scratch determines the quality of protection against corrosion. Ideally, a protection system should release inhibitor to the scratch shortly after the coating has been damaged to ensure immediate protection. After a prolonged period, the rate of the supply of inhibitor should decrease to avoid loosing all of inhibitor from a location next to a scratch, and an excess of inhibitor that does not react with the exposed surface. Experimental studies have demonstrated that the efficiency of protection against corrosion is strongly dependent on the particular composition of an organic coating. An inhibitor that is highly effective in a certain matrix can have undesired properties in another matrix [15–17]. Various inhibitor release modes have been discovered [10–19] depending on the actual composition of the coating, i.e., the type of inhibitor and polymer matrix involved. Although release controlled by a Fickian diffusion process (i.e., the total mass M_I of inhibitor released to a scratch proportional to the square root of time t) has been observed in some experiments; other results have also been reported ($M_I \sim t^{\alpha}$, with $0.25 \leqslant \alpha \leqslant 1$). Furman et al. [16] found that the release of chromates is described

---

* Corresponding author.
E-mail address: ztabor@pk.edu.pl (Z. Tabor).

http://dx.doi.org/10.1016/j.corsci.2014.01.026

by a non-Fickian release ($t^{0.25}$). Nazarov et al. [17] reported that the leaching rate of the same corrosion inhibitor in a different matrix was logarithmic, while the release of phosphate was closer to $t^{0.25}$ and the release of tungstate closer to linear (t^1).

A thorough understanding of the origin of the diversity of the release modes is necessary for the design of protective organic coatings with the desired release characteristics. A few theoretical models that involve various electrochemical processes have been proposed to describe the dynamics of inhibitor release in specific coating systems [12,20]. However, as far as we know, the problem how to design a system with a specific release rate has been quantitatively addressed in a single study of Javierre et al. [21]. In particular, Javierre et al. [21] showed that some non-random distributions of inhibitor particles within the matrix can lead to a non-Fickian ($M_I \sim t^{\alpha}$, with $\alpha \geqslant 0.5$) release dynamics.

Although the approaches proposed in the aforementioned studies are important, other explanations of non-Fickian behavior should also be considered. Primarily of all, different release modes can be qualitatively attributed to either diffusion or inhibitor dissolution, which are the rate-determining processes of release. A quantitative model based on this conjecture and interpolating between Fickian and non-Fickian release has not been proposed so far. Consequently, the present paper is focused on modeling conditions that lead to the non-Fickian release of inhibitor from a damaged coating to a scratch. In particular, we propose a model that considers the nonlinear coupling between the concentration of an inhibitor release-triggering species penetrating the organic matrix and the release rate of the inhibitor to the matrix. Although, in general, the transport of species in organic matrices depends on their structure and the interaction between the diffusing species and polymer chains [22], which has led to anomalous diffusion in some cases [23], we assumed that Fickian diffusion process controls the transport of species. This assumption is justified, for example, by epoxy systems [24] or rubbery polymers [25]. It follows from the numerical simulations that the release of the inhibitor to a scratch can be controlled in a wide range of rates by proper tuning of a few model parameters.

2. The mathematical model

In the present study the process of inhibitor release to a scratch was modeled for two- and one-dimensional systems. It was assumed that an inhibitor release-triggering species penetrated the coating from a scratch, which is a reasonable assumption if inhibitor release is triggered, for example, by an increased concentration of corrosion products. Change of pH can be used as an internal trigger for the release of inhibitors as, for example, during localized corrosion of steel [26] or aluminum [27] the anodic area often has an acidic pH and the cathodic area has an alkaline pH. In the case of typical multilayer coatings it can be reasonably assumed that the diffusion from the external surface of the undamaged coating (top coat), with good barrier properties, is much slower than the diffusion from a scratch.

The release of inhibitor from a damaged coating to a scratch is modeled by the following coupled equations, which are defined over a domain composed of a finite size scratch ($0 \leqslant x \leqslant r_s$, $0 \leqslant y \leqslant y_{max}$ where x and y are space coordinates, r_s is a half-size of the scratch, and y_{max} is thickness of the scratch) and semi-infinite ($x > r_s, 0 \leqslant y \leqslant y_{max}$) coating (see Fig. 1 for a schematic draw of the analyzed system):

$$c_{M,S}(x,t) = C_M \qquad 0 \leqslant x \leqslant r_s \tag{1}$$

$$\frac{\partial c_{M,C}}{\partial t}(x,t) = D_{M,C} \cdot \nabla^2 c_{M,C}(x,t) \qquad x > r_s \tag{2}$$

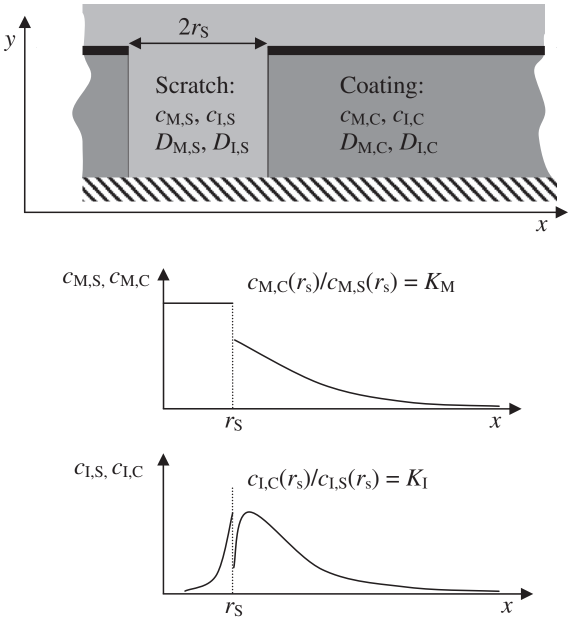

Fig. 1. A schematic of the modeled one-dimensional system.

$$\frac{\partial c_{I,S}}{\partial t}(x,t) = D_{I,S} \cdot \nabla^2 c_{I,S}(x,t) \qquad 0 \leqslant x \leqslant r_s \tag{3}$$

$$\frac{\partial c_{I,C}}{\partial t}(x,t) = D_{I,C} \cdot \nabla^2 c_{I,C}(x,t) + P(c_{I,C}, c_{M,C}, c_P) \qquad x > r_s \tag{4}$$

$$\frac{\partial c_P}{\partial t}(x,t) = -P(c_{I,C}, c_{M,C}, c_P) \qquad x > r_s \tag{5}$$

where $c_{M,S}$ and $c_{M,C}$ are the concentrations of an inhibitor-release triggering species in the scratch and in the coating, and $c_{I,S}$ and $c_{I,C}$ denote the respective concentrations of inhibitor outside inhibitor reservoirs. We assumed that the concentration $c_{M,S}$ of the inhibitor-release triggering species in the scratch is constant and equal to C_M (Eq. (1)). This assumption reflects a case of a coating immersed in a corrosive environment, in which case the inhibitor-release triggering species diffuse constantly into the scratch from the surrounding environment. Because the diffusion of such species within the external corrosive environment is typically much faster than the diffusion within the coatings, it can be reasonably assumed that the variations of these species within the scratch can be neglected. The transport of all species is described by Fickian diffusion (Eqs. (2)–(4)). To account for a finite capacity of the inhibitor reservoirs, the concentration $c_P(x > r_s, t)$ of the inhibitor within the reservoirs was also introduced (Eqs. (4) and (5)) with $P(c_{I,C}, c_{M,C}, c_P)$ being some function which specifies how the release rate depends on c_P, $c_{I,C}$ and $c_{M,C}$. The parameters $D_{M,C}$ and $D_{M,S}$ are the coefficients of diffusion of the inhibitor-release triggering species in the coating and in the scratch, respectively; the parameters $D_{I,C}$, $D_{I,S}$ are the coefficients of diffusion of the inhibitor in the coating and the scratch, respectively.

The inhibitor is released locally in the coating and we assumed that the rate of this process depends nonlinearly on the concentration of the inhibitor and the inhibitor-release triggering species in accordance with the Noyes–Whitney equation [28]. In particular, we assumed that the release rate $P(c_{I,C}, c_{M,C}, c_P)$ of the inhibitor is given by the following formula:

$$P(c_{I,C}, c_{M,C}, c_P) = \begin{cases} b\left(1 - \frac{c_{I,C}}{a c_{M,C}}\right) & c_{I,C} \leqslant a c_{M,C} \quad \text{and} \quad c_P > 0 \\ 0 & c_{I,C} > a c_{M,C} \quad \text{or} \quad c_P = 0 \end{cases} \tag{6}$$