



Corrosion of single layer thin film protective coatings on steel substrates for high level waste containers



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ABSTRACT

Single-layer thin film coatings have been deposited on steel substrates and tested for their corrosion resistance. These coatings include TiN, ZrO₂, TiO₂, Al₂O₃, and MoS₂, and it is proposed that they will act as barriers to provide protection to the steel canisters that are part of the dry cask storage system for high level nuclear waste. Corrosion testing was completed using electrochemical potentiodynamic polarization techniques in aerated 1 M NaCl solution. Results show an exponential increase in corrosion rate with increasing temperature and an exponential decrease in the passive breakdown overpotential, which is directly related to the ability of a material to form and sustain a corrosion-inhibiting passive film in a given environment. Additionally, kinetic activation parameters have been experimentally determined for each material, leading to predictive equations for corrosion rates. The bare and coated samples corrode analogously, indicative of pores allowing the coating and substrate to corrode simultaneously. The samples were also placed in circulating salt brines of varying pH as a supplementary corrosion testing mechanism to explore their corrosivity over extended time. Negligible weight change was experienced by the bare and coated steel samples over a period of 5 months. Increasing the coating thickness and the number of layers may provide higher resistance to uniform and localized corrosion.

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1. Introduction

Storage of spent nuclear fuel from commercial reactors is one of the most important issues facing the nuclear industry. Spent fuel is classified as high-level waste (HLW), which makes up more than 99% of the total radioactivity contained in all forms of nuclear waste, and thus requires the most stringent control on performance of storage containers (Yim and Murty, 2000). HLW storage containers are required to provide complete containment for up to 1000 years, after which very slow release of radionuclides is permitted, in accordance with NRC rule 10CFR60 (Farmer et al., 1991; Beavers et al., 1985). On site dry cask storage is the only long term storage option for nuclear fuel removed from commercial light water reactors (LWRs). Dry storage casks consist primarily of a steel canister and concrete overpack, often with additional layers in between for neutron and gamma shielding (Bare and Torgerson,

2001).

HLW canisters are typically made of stainless steel because of its good mechanical strength and corrosion resistance stemming from its ability to readily form passive surface films (Yim and Murty, 2000; Farmer et al., 2003; Lambert et al., 2012). Being an austenitic material, it is not susceptible to catastrophic brittle failure as are ferritic steels. However, stainless steel suffers from localized corrosion when exposed to various environments. By its nature, localized corrosion is random and volatile. Coupled with an overall lack of in-situ monitoring for HLW storage, the service life of the dry storage canisters is very difficult to predict.

The primary types of localized corrosion that plague stainless steel are intergranular corrosion and stress corrosion cracking (SCC), both of which have the potential to greatly shorten the useful life of spent fuel canisters. Chromium depletion due to carbide buildup at grain boundaries often leads to fissure via intergranular corrosion in stainless steels. This failure mechanism is a greater issue in the presence of ionizing radiation, which causes voids and cavities leading to further depletion of chromium along grain boundaries (Revie and Uhlig, 2008). SCC is a method of crack

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initiation and/or growth involving a tensile stress of sufficient magnitude and an aggressive environment. For steel canisters, failure is most likely to occur through and near welded regions as they contain residual stresses from the welding process that are generally sufficient to cause SCC (Kosaki, 2008; Kunerth et al., 2012). The principle environments causing localized corrosion in stainless steels are chloride-based due to chloride ions promoting pitting corrosion per localized passive film breakdown, which, when paired with the appropriate stress field, may lead to SCC (Revie and Uhlig, 2008). Most of the environments to which waste canisters could potentially be exposed are chloride-containing (sea water, sea air, geological brines, etc.). Thus, chloride ions pose a threat to the long term integrity of HLW storage containers.

An alternative to stainless steels that has been considered and studied in the past is carbon steel. Carbon steel is known to corrode more readily than stainless steel but is more resistant to localized attack. Carbon steel lacks the ability to form full protective passive films under normal circumstances in most environments, which is the basis for the excellent corrosion resistance of stainless steel. However, localized corrosion is much more severe when a very protective surface layer is penetrated because the local attack can be sustained (Marsh and Taylor, 1988). Owing to this, carbon steel is not generally plagued by localized corrosion, as is the bane of stainless steel. However, carbon steels are still susceptible to localized corrosion, particularly SCC in carbonate, nitrate, and caustic environments (Beavers et al., 1985). The residual stress can be mitigated with stress relief heat treatment such that SCC is not of great concern. This is seldom practical for stainless steels, as the threshold stress for SCC of carbon steels is much higher than for austenitic steels (Cottis, 2000). Moreover, SCC will typically not occur when there is significant uniform corrosion, as with carbon steel.

In order to combat premature failure of steel waste canisters, various thin-film inorganic coatings have been proposed. These coatings include TiN, ZrO₂, TiO₂, Al₂O₃, and MoS₂ and have been shown to be good barriers to localized corrosion and hydrogen diffusion (Checchetto et al., 1996; Scheffing et al., 2006).

In this study, these coatings are deposited on 1" diameter steel disks in single layers using non-reactive magnetron sputtering techniques. The oxide coatings (ZrO₂, TiO₂, and Al₂O₃) deposit very slowly and have a maximum thickness below 100 nm. The remaining non-oxide coatings (TiN and MoS₂) can be deposited more quickly, resulting in a maximum thickness of approximately 500 nm. Coating thicknesses have been measured using focused ion beam (FIB) milling techniques Stainless steel type 316 and 304, along with A36 low-alloy carbon steel with and without thin film coatings have been subjected to electrochemical polarization techniques and circulating salt brines in order to characterize uniform and localized corrosion, among other properties.

2. Theory

2.1. Electrochemical corrosion

Electrochemical measurements allow corrosion to be observed and quantified over a much shorter timescale than would be necessary in the absence of applied bias (polarization) and subsequent response current (Dean, 1986).

The Butler–Volmer (Eq. (1)) is often used to describe the relationship between potential and current for a system undergoing a combination of anodic and cathodic electrochemical reactions. The quantity $2.3 RT/\alpha nF$ is customarily denoted as β (Petrii et al., 2007), in which case (1) may be rewritten as shown in (2). This gives a relationship between the applied current and the deviation from the equilibrium potential (overpotential) in terms of parameters

characteristic of the coupling of the material and environment (corrosion current and Tafel slopes).

$$I = I_{corr} \left(\exp \left[\frac{\alpha_a n F (E - E_{corr})}{RT} \right] - \exp \left[\frac{-\alpha_c n F (E - E_{corr})}{RT} \right] \right) \quad (1)$$

Where: α_a , α_c are anodic and cathodic charge transfer coefficients.

F is Faraday constant

n is the number of electrons involved in electrode reaction

R is the universal gas constant

T is absolute temperature, K

E_{corr} is the corrosion (equilibrium) potential, V

E is the potential, V

I_{corr} is the corrosion (equilibrium) current, A

and I is the current, A

$$I = I_a + I_c = I_{corr} \left(e^{2.3\eta/\beta_a} - e^{-2.3\eta/\beta_c} \right) \quad (2)$$

Where: I_a , I_c are anodic and cathodic currents, A.

η is the overpotential ($\eta = E - E_{corr}$), V

β_a , β_c are anodic and cathodic Tafel slopes, V/decade

By restricting the potential to a region very close to the corrosion or equilibrium potential (low overpotential region), the exponentials can be expanded in a Taylor series about $\eta = 0$, resulting in the Stern–Geary equation (Stern and Geary, 1957):

$$\left. \frac{d\eta}{dI} \right|_{\eta \rightarrow 0} = \frac{\beta_a \beta_c}{2.3 I_{corr} (\beta_a + \beta_c)} \quad (3)$$

The left hand side of (Eq. (3)) is the slope of the potential versus current curve in the immediate vicinity of the equilibrium potential and is known as the polarization resistance, R_p .

In the high overpotential region, it is simple to show that either the anodic or cathodic reaction dominates. The region of high positive overpotential, $\eta > 0$, is dominated by the anodic reaction, whereas in the high negative overpotential region, $\eta < 0$, the cathodic reaction dominates. For anodic current (Eq. (4)):

$$I = I_a = \exp \left(\frac{2.3\eta}{\beta_a} \right) \quad (4)$$

Rearranging (Eq. (4)), the overpotential can be written as:

$$\eta = a + b \log(I) = \frac{\beta_a}{2.3} [\ln(I) - \ln(I_{corr})] \quad (5)$$

Therefore, the anodic Tafel coefficient, β_a , is proportional to the slope of the voltage versus log current curve in the region of positive overpotential. The same applies for the cathodic Tafel coefficient, β_c , in the negative overpotential region.

Rearranging (Eq. (3)) to solve for corrosion current gives:

$$I_{corr} = \frac{\beta_a \beta_c}{2.3 R_p (\beta_a + \beta_c)} \quad (6)$$

All terms on the right hand side of (Eq. (6)) can be determined experimentally, in which case the equilibrium current is immediately obtainable. Once the corrosion current has been calculated (Eq. (7)), can be used to relate corrosion current to corrosion rate for a given material undergoing electrochemical corrosion.

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