

Oxidation of Carbon Steel under Gamma Radiation Conditions

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1. Introduction

The effect of ionizing radiation on materials corrosion, in particular, via its effect on the aqueous redox condition, is an area of uncertainty for the nuclear power industry. We have been investigating the corrosion kinetics of carbon steel as a model material, and the effect of γ -irradiation on the kinetics, as a function of pH, temperature, surface film composition, and dissolved chemical species using various electrochemical, surface, and chemical speciation analyses. The corrosion kinetics were studied by monitoring the corrosion potential (E_{CORR}) in-situ, and cyclic voltammetry was used to aid in the characterization of oxide growth/formation as a function of potential. The surfaces were also examined using SEM, XPS, and Raman spectroscopy. Preliminary results indicate that gamma irradiation increases the corrosion potential from a region where the anodic oxidation is limited to $\text{Fe}(\text{OH})_2$ and Fe_3O_4 to a region where the oxidation of $\text{Fe}(\text{OH})_2$ to $\gamma\text{-FeOOH}$ and Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$ is possible.

2. Methods and Results

2.1 Oxidation Regions of Carbon Steel

Previous studies on carbon steel corrosion in borate solutions at pH 10.6 and room temperature have observed three distinct potential ranges for oxide formation based on various electrochemical and surface analytical measurements [1,2].

Ox I ($E \leq -0.7$ V vs SCE), the main oxide formed is Fe_3O_4 , which grows via a solid-state process, except that in the very early stages of film formation highly soluble Fe^{II} oxides/hydroxides may be formed;

Ox II (-0.5 V $\leq E$ (vs SCE) ≤ -0.1 V), continuous growth of the Fe_3O_4 layer is accompanied by its anodic conversion to a more maghemite ($\gamma\text{-Fe}_2\text{O}_3$)-like phase near, or at, the oxide/solution interface by a similar solid-state mechanism; and

Ox III (0.0 V $< E$ (vs SCE) < 0.4 V), the anodic conversion of this $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ oxide to $\gamma\text{-FeOOH}$ leads to structural changes, which can induce micro-fracture.

2.2 Electrochemical Analysis under Gamma Radiation

A three-electrode cell consisting of a reference electrode, a Pt mesh counter electrode and a carbon steel working electrode was used for electrochemical measurements. All potentials in this study are quoted on the SCE scale (0.242 V vs. SHE). The working electrode in all experiments was ASTM A516 Gr70 carbon steel. The cell was either placed inside the sample chamber of a ^{60}Co gamma irradiator (Gammacell 220 Excel, MDS Nordion, Kanata, ON) or on a benchtop (for experiments without irradiation). The γ -radiation dose rate in the Gammacell was ~ 6.2 $\text{kGy}\cdot\text{h}^{-1}$.

Gamma irradiation decomposes water into a range of redox active species ($\bullet\text{OH}$, H_2O_2 , O_2 , $\bullet\text{O}_2^-$, etc) [3-5] and its main effect is to increase the electrochemical potential at the aqueous and surface interface, or corrosion potential. At room temperature and pH 10.6 the corrosion potential, E_{CORR} , attains a steady-state value of ~ -0.65 V in de-aerated solutions in the absence of irradiation, regardless of the presence of any pre-existing oxides formed by anodic pretreatments [2,6]. The corrosion potential varies with temperature, but remains in region Ox I. Exposing the system to γ -radiation increases E_{CORR} quickly to ~ 0 V, a potential in region Ox II, regardless of the initial oxide pretreatment process. The increase in E_{CORR} from region Ox I to Ox II affects the chemical composition of the oxide film formed on carbon steel. Based on the E_{CORR} measurements, along with other electrochemical measurements and XPS analysis, we have concluded that the oxide formed in the absence of radiation is mainly Fe_3O_4 , while the oxide formed under irradiation has a mixed $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ structure [2,7].

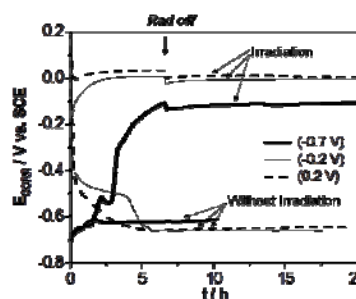


Fig. 1. Corrosion potential as a function of time during and after 6 h irradiation, and without irradiation in 0.01 M borate solutions at pH 10.6. Prior to the E_{CORR} measurement, oxide films were grown potentiostatically at 0.2 V, -0.2 V, or -0.7 V.

2.3 Surface Analysis Studies

The tests span a temperature range from 25°C to above the boiling point of water at atmospheric pressure. For the high temperature experiments, a special apparatus was used to prevent failure of the electrode cell by overpressurization. In each experiment a coupon of ASTM A516 Gr70 carbon steel was placed inside a glass vial (20 mL total volume) and the test solution was added to the vial until the coupon was fully submerged. The vial was capped to provide a gas leak tight seal. Up to four vials at a time, each containing one steel coupon, were loaded into a 250 mL type 316 stainless steel pressure vessel and water was added to partially fill the vessel (external to the sealed vials). The pressure vessel was then sealed and placed inside an electric heating mantle with a temperature regulator. The vessel and heater were either irradiated and heated to a specific temperature, or just heated. During a test the apparatus was held at a constant temperature for up to 7 days. The coupons were then analyzed using various surface analytical techniques and the pH of the solution in the vial was measured.

Results show that continuous irradiation enhances surface oxide formation with the type of oxide formed dependant on the solution pH [7]. For experiments at 150°C and a $[\text{OH}^-]$ equivalent to that for $\text{pH}_{25^\circ\text{C}} = 10.6$, the surface oxide on carbon steel after γ -irradiation was non-porous and uniform, and no localized corrosion was observed. This oxide, however, appears to be susceptible to brittle fracture during cooling. Raman spectroscopy of the surface film indicates that it is a mixture of the phases of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. In contrast, at 150°C with $[\text{OH}^-]$ equivalent to neutral $\text{pH}_{25^\circ\text{C}}$, metal dissolution is significant and the surface oxide film is very porous. Raman spectra show that this oxide film is also composed of a mixture of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. The results from this work combined with the electrochemical studies of the same system as a function of pH and temperature can be used to deconvolute the effects of radiation, pH and temperature on the nature of the corrosion process.

(b) digital photographs of the solutions in the test vials taken before the coupons were removed.

3. Conclusions

Variation in system temperature and pH may affect rates of oxide film growth and dissolution but do not play a significant role in altering the chemical composition of the oxide film or the E_{CORR} potential at temperatures up to 150°C and pH values between neutral and mildly basic. However, γ -radiation has a major impact, increasing E_{CORR} and therefore determining which oxide phases form on the steel surface. Specifically, irradiation leads to the formation of a more passive film composed of a mixture of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$.

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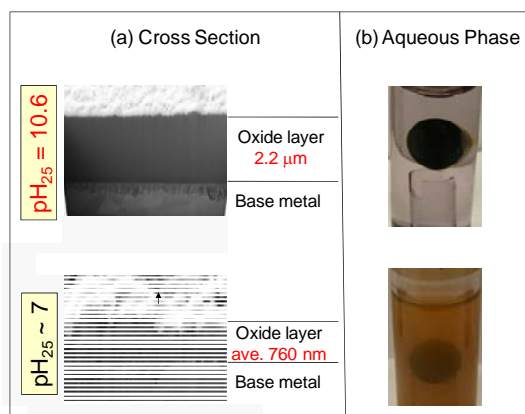


Fig. 2. a) SEM images of the cross sections of coupons irradiated for 66 h at 150°C and $\text{pH}_{25^\circ\text{C}} 10.6$ or $\text{pH}_{25^\circ\text{C}} \sim 7$, and