FILM BREAKDOWN PROCESSES ON CARBON STEELS IN THE PRESENCE OF LARGE ANIONS

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Abstract

The objective of this research is to determine the features, which cause film breakdown leading to pitting in solutions containing halide anions. It is commonly accepted that the influence of Cl^- on passive film properties is the key feature in breakdown, and the possibility that transformations in the oxide are responsible has not been considered. While variations in breakdown potential are observed in the presence of the different halide anions, the key feature leading to breakdown appears to be subtle changes in oxide structure/composition.

1. Introduction

Carbon steel is a common structural material used in various nuclear facilities, and corrosion of carbon steel is an important operational and safety issue for the nuclear industry. The factors affecting the corrosion rate of steel include the surface-oxide film composition and morphology and the aqueous redox and chemical environment. This project concerns the effects of large halide anions on pitting corrosion. It is commonly accepted that the influence of Cl^- on passive film properties is the key feature in breakdown, and the possibility that transformations in the oxide are responsible has not been considered.

Electrochemical techniques such as electrochemical impedance spectroscopy (EIS), cyclic voltammetry and amperometry, and surface analytical methods such as SEM and in-situ/ex-situ Raman spectroscopy have been used to investigate the changes in film properties leading to breakdown in borate buffered solutions containing Cl^-, Br^- and I^-.

2. Experimental

2.1. Electrochemical cell and electrodes

A standard three-electrode, glass electrochemical cell was used in this study. The cell contained a carbon steel working electrode (WE), saturated calomel reference electrode (SCE, 0.241 V vs. SHE), platinum wire mesh counter electrode (CE, area = 18 cm^2), and a gas dispersion tube. The WE was fabricated from A516 Gr70 carbon steel, with a composition in wt% of C 0.28, Mn 1.3, P 0.035, S 0.035, Si 0.45, and balance Fe. All potential measurements were made with an 8-channel Solarton model 1480 potentiostat and are quoted on the SCE scale.

2.2. Solutions

All solutions were prepared using Milli-Q Millipore (de-ionized) water. Solutions for electrode pre-oxidation were prepared with reagent-grade sodium tetraborate (99.0% assay) to a concentration of 0.01 M $Na_2B_4O_7.10H_2O$. Iodide, bromide and chloride solutions in the concentration range of 10^{-4} to 10^{-3} M were prepared with reagent-grade salts (99.0% assay).

2.3. Experimental procedure

All experiments were conducted at room temperature. Cyclic Voltammetry Measurements (CV) were conducted between the cathodic cleaning potential and various anodic limits at a scan rate of 5 $mV \cdot s^{-1}$. For the potentiostatic measurements, after 5 minutes of cathodic cleaning at E = -1.1 V, the potential was stepped to E = -0.5 V, then swept to E = -0.3 V at 0.5 $mV \cdot s^{-1}$. Then the potential was increased in 20 mV increments, with the potential held for 20 minutes at each value to allow oxide film growth. Each potential step was followed by an EIS experiment. The potential was increased up to +0.4 V or until the film breakdown occurred. Finally, a potentiodynamic scan from either E = 0.4 V, or from a potential after film breakdown, to E = -0.5 V at 5 $mV \cdot s^{-1}$ was done. This experiment was performed in halide-free borate-buffered solutions and also in buffered solutions containing different halides at various concentrations.

3. Results

3.1. Film Breakdown During Cyclic Voltammetry Scans

Figure 1 shows the effect of halide anions on the CV recorded on carbon steel. The voltammograms of the first forward scans in halide solutions are identical up to a potential of 0.1 V, above which the anodic current deviates from that measured in borate-only. This increase in current indicates that the surface oxide film has been breached and pitting has occurred. The potential at which the anodic current starts to deviate from that observed in borate-only solution will be referred to as the film-breakdown potential, E_B, hereafter. The film breakdown potential observed varies slightly, but the variation is stochastic and does not depend on the nature of the halide; the observed E_B values in this set of experiments are 0.13 V for Br^-, 0.18 V for Cl^- and 0.28 V for I^-. On the reverse scan, as the potential decreases, the current maintains a higher

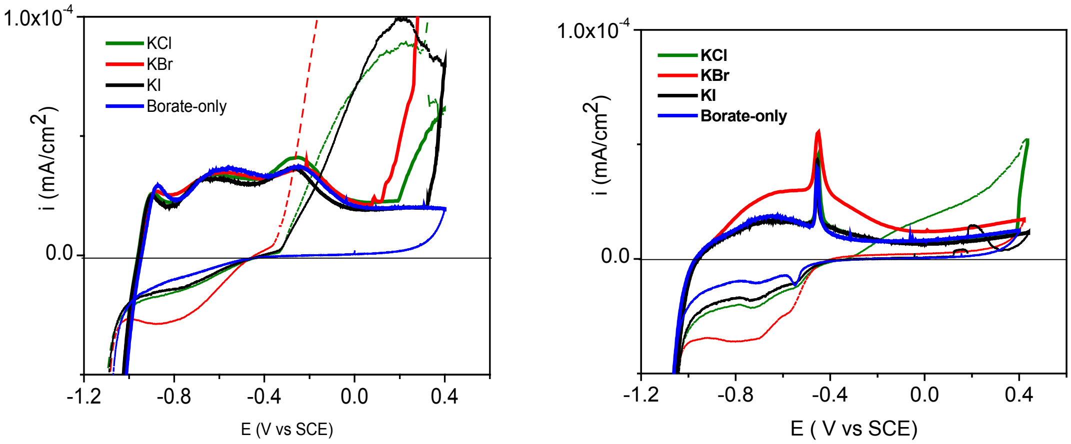

Figure 1: Cyclic voltammograms recorded on carbon steel in 0.01 M borate buffer solutions containing 10^{-3} M halide: (a) the first cycle and (b) the second cycle

anodic value than on the forward scan before eventually switching to cathodic. The potential at which the current becomes zero was observed to be the same at -0.45 ± 0.02 V for all three halides. This potential will be referred to as the zero-current potential, E_{zero}.

The magnitude of the anodic current following the film breakdown on the forward scan depended strongly on the type of halide, and also varied from one experiment to another. The cathodic current observed below E_{RP} was also slightly larger in the presence of halides than in the halide-free solutions. The CVs obtained on subsequent cycles observed in the presence of halides are practically the same as those of the borate-only case, except when Cl^- was present. For the Cl^- case, film breakdown was observed again on the second scan, but at a higher E_B than observed on the first cycle. No breakdown behaviour was observed on the third cycle, even for the Cl^- case. E_{zero} did not change with the number of scan cycles, remaining at -0.45 ± 0.02 V in all cases. No film breakdown was observed during CV scans when the halide concentration was below 10^{-4} M.

3.2. Potentiostatic Film Growth and Breakdown Measurements

Two sets of experiments were performed; in the first set, halide was added from the onset, and in the second set halide was added after the film growth potential had reached a value > 0.14 V. In general, each time the potential was increased (in 20 mV steps) as shown in Figure 2, the current initially jumped to a slightly higher value but immediately returned to the value it had prior to the increase in potential. However, in the experiments that resulted in pitting, above a certain potential the current jumped to a higher level and remained at the high value or decreased, but at a much slower rate. The potential at which this change occurs is taken as E_B.

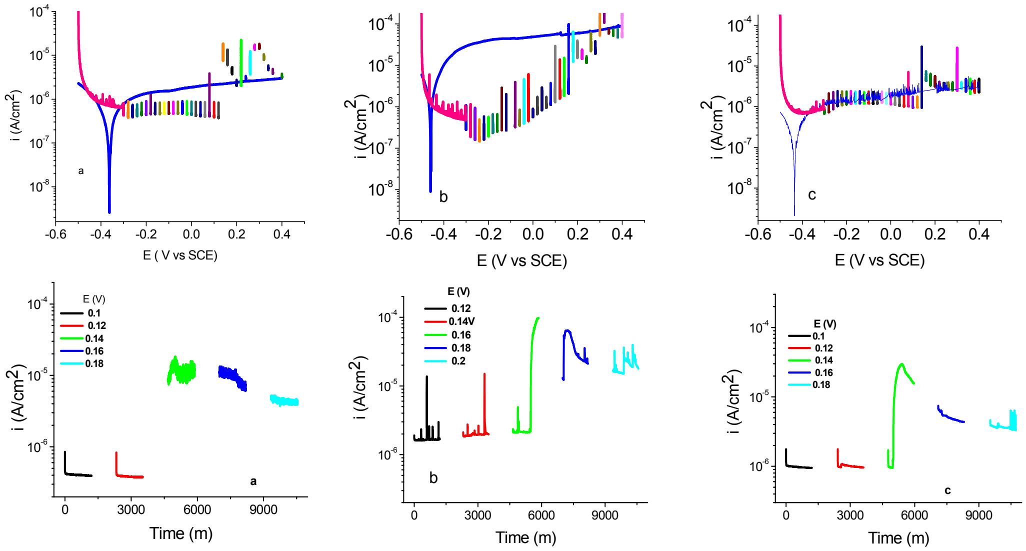

Figure 2 Currents measured during potentiostatic film growth using the potential profile

E_B varied somewhat from one experiment to another, but did not appear to depend on the type of halide. Furthermore, the film breakdown, if it occurred, was only observed for E ≥ 0.08 V.

The histogram in Figure 3 shows that the lowest E_B recorded so far was 0.08 V. More experiments are being carried out in order to unambiguously determine the minimum value of E_B. The current level following the breakdown varied considerably from one experiment to another, suggesting that once film breakdown occurred and pitting initiated, the rate of propagation of the pit depends strongly on the local pH and redox environment inside the pit.

In the experiments that did not result in pitting, a higher surge of current was often observed on increasing the potential to E ≥ 0.08 V (i.e., to the minimum). However, the current quickly decreased back to the potential-independent value, as observed at other potentials. This suggests that film breakdown might have been initiated but was quickly repaired, preventing the propagation of pitting.

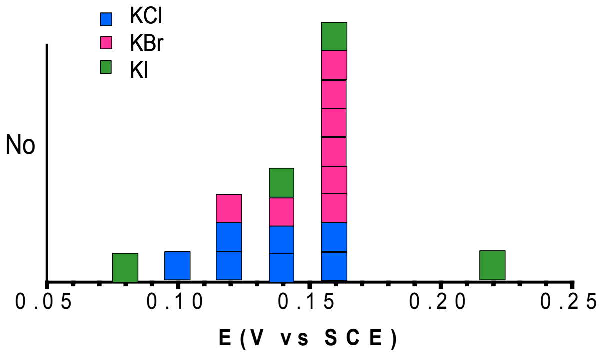

Figure 3: Histogram of breakdown potentials, E_B , in different halides.

The above results indicate that halides could facilitate pitting corrosion in two ways:

1) They could be incorporated in the metal-oxide matrix during the oxide film formation, resulting in highly defective films which break down and initiate pitting under appropriate conditions (i.e., a sufficiently high potential).

2) They are not involved in the oxide film formation, but once film restructuring leading to breakdown and exposure of the base metal occurs at high potential, they take advantage of film defects, prevent repairing, and thereby allow pitting to initiate.

To differentiate between these possibilities, halide was added at a later stage during the film growth in the second set of the stepwise potentiostatic experiments. In these experiments, the oxide-film was initially grown in borate-only solution using the same potential profile used in the first set of experiments (Figure 1). When the film growth potential reached a desired value, 10^{-3} M halide was added, and the potential maintained at this value over a long period. This long period was used to ensure similar kinetic conditions (i.e., a similar exposure time to the halide solution) in the two sets of experiments. The addition of halide at potentials below 0.1 V did not lead to film breakdown and pitting, even though the potential was maintained at a given value for up to 20 hours. However, the addition of halide at E > 0.14 V often led to pitting. Figure 4 shows the result of such an experiment in which 10^{-3} M Br^- was added to the solution once E reached 0.14 V. Following Br^- addition, the potential was increased to 0.16 V and maintained at this value for 5 h. In this particular experiment, two current excursions occurred, the first at about 1 h and the second at about 3 h after the Br⁻ addition. These sharp increases in current indicate film breakdown. However, in the first event, breakdown did not result in pitting, whereas in the second event it did.

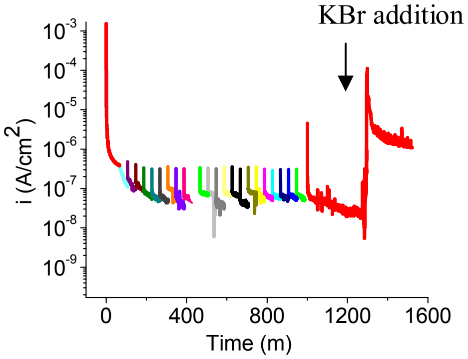

Figure 4: Current observed during potentiostatic film growth. 10^{-3} M KBr was added to the borate solution when E reached 0.14 V. Following the Br^- addition, the potential was increased to 0.16 V and maintained at this value for 5 h.

5. Summary

Pitting is a probabilistic event, which can be treated as occurring in two distinct steps of initiation and propagation. The goal of my research is to establish the mechanism and the conditions for pit initiation on carbon steel in the presence of halides. So far, I have studied the process as a function of the type and the concentration of halide while electrochemically growing the oxide film. The extent of pitting depended considerably on the type and concentration of halide, presumably due to the differences in their roles in pit propagation. However, pitting was never observed when the oxide film was grown at electrochemical potentials below 0.0 V (vs. SCE). Although I need to build a statistically significant database to be conclusive, the results obtained so far suggest that the conversion of Fe_3O_4 to γ-FeOOH may be responsible for the film breakdown, which can lead to pitting.

6. Acknowledgements

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