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Electrochemical Studies of Nitrate-Induced Pitting in Carbon Steel

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Abstract

The phenomenon of pitting in carbon steel exposed to alkaline solutions of nitrate and chloride was studied with the cyclic potentiodynamic polarization technique. Open-circuit and pitting potentials were measured on specimens of ASTM A537 carbon steel in pH 9.73 salt solutions at 40°C, with and without the inhibiting nitrite ion present. Nitrate is not so aggressive a pitting agent as is chloride. Both nitrate and chloride did induce passive breakdown and pitting in nitrite-free solutions, but the carbon steel retained passivity in solutions with 0.11-M nitrite even at a nitrate concentration of 2.2 M.

Keywords: Localized corrosion, cyclic potentiodynamic polarization, passivity, chloride

Introduction

As a result of reprocessing nuclear fuel and target elements with nitric acid, the United States Department of Energy has generated nitrate-bearing high-level radioactive waste. Much of this waste is stored in carbon steel tanks, after having been made alkaline with substantial additions of sodium hydroxide. Carbon steel is essentially immune to uniform corrosion in this environment, but it is susceptible to localized corrosion in the forms of stress corrosion cracking and pitting, depending on the temperature and the specific waste chemistry. In addition to the nitrate ion, the waste may also contain chloride and sulfate that can induce localized corrosion. The initiation of localized corrosion in the carbon steel-waste environment can be prevented by nitrite in combination with a minimum pH or hydroxide concentration.[1,2,3]

The possibility of pitting of carbon steel by the nitrate ion is a particular concern as high-level radioactive waste at the Department of Energy's Savannah River Site is diluted (washed) in preparation for its solidification in a glass waste form. Nitrate-induced pitting has therefore been extensively studied in laboratory testing of dilute (hydroxide and nitrate concentrations < 1 molar) simulated radioactive waste solutions. This work has been empirical in nature, and employed the cyclic potentiodynamic polarization (CPP) and coupon immersion techniques to identify pitting and non-pitting waste compositions. CPP scans were examined for the hysteresis in the response of the current density to the applied potential, and coupons were examined microscopically for pits. The nitrite concentration of the test solutions was varied, and the minimum nitrite concentration that prevented pitting initiation was determined. This minimum nitrite concentration was found to vary linearly with the concentration of the test solution and to depend on the Celsius temperature exponentially.[3] When nitrate, chloride, or sulfate was varied independently of the other waste simulant components, the familiar linear relationship[4] was found between the logarithm of the inhibiting nitrite concentration and the logarithm of the aggressive species concentration.[2] Nitrate controls the minimum nitrite requirement to prevent pitting in certain high-level radioactive waste solutions because it is the most abundant aggressive ion in those solutions.

The detailed mechanism of the inhibiting action of nitrite in the presence of nitrate ions is not well understood. Indeed much of the corrosion literature is concerned with the role of chloride in the localized breakdown of passivity.[5] The goal of the present work was to measure the basic pitting-related electrochemical potentials of the nitrate-nitrite-A537 carbon steel system at a pH and temperature typical of a dilute high-level waste environment (pH 9.5 to 10.5 and 40 to 50°C) . Instead of complex simulants of high-level radioactive waste, the experiments employed simple alkaline solutions containing various concentrations of nitrate and nitrite. Chloride solutions were also investigated, to provide a comparison with the nitrate behavior. Open-circuit, pitting or breakdown, and some repassivation potentials were measured. The effect of nitrite on these potentials was studied by including nitrite at a concentration of 0.11 M and by eliminating nitrite from the test solutions.

The results of the present measurements will be incorporated into a larger experimental and modeling effort to explain the mechanism of nitrite pitting inhibition. The ultimate goal is an improved understanding of the nitrate-induced pitting phenomenon that may lead to superior corrosion prevention measures in the storage and processing of liquid radioactive waste.

Experimental

Electrochemical potential measurements were obtained with the cyclic potentiodynamic polarization (CPP) technique, which has been the subject of recent reviews.[6,7] CPP scans were obtained with a computer-controlled potentiostat. Potential was measured with a saturated calomel electrode. The scans were started at -50 mV with respect to the open-circuit potential. The specimens were equilibrated in the heated test solutions for 5.5 hours before initiating the scan. Figure 1 shows the typical increase of the open-circuit potential with time, which continued in some instances even after 16 hours. The chosen delay of 5.5 hours allowed the collection of data in an acceptable period of time, while it permitted the specimen to experience the substantially greater part of the approach to equilibrium. The potential was swept at a constant rate of 0.5 mV/sec and reversed upon attaining a current density of 1 mA/cm^2. The scan was terminated at 0 mV with respect to the original open-circuit potential.

All experiments were conducted with ASTM A537 class 1 carbon steel (a waste tank material of construction) discs 1.6 cm in diameter and 2.0 cm^2 of wetted surface area. A copper wire was attached with a conductive epoxy adhesive to the rear face of a disc for electrical contact, and the disc was set in an epoxy metallurgical mount (Figure 2). This method allowed the mounted specimen to be easily handled for grinding and polishing to a 1-micron finish. A single disc was repeatedly polished and used for many tests. The metallurically mounted disc with a 1-micron finish is believed to yield a more consistent open-circuit potential value than that obtained with the customary 600-grit finish of a disc held in a commercial flat-specimen holder. Figure 3 shows the reproducibility obtainable in the CPP scans; the open-circuit potential for the four tests plotted varied from -63 mV to -118 mV vs. SCE.

Solutions were prepared from reagent-grade chemicals and distilled water. Sodium salts were used to introduce the nitrate, nitrite, and chloride ions. The initial pH of the solutions was set at 9.73 ± 0.05 through an equilibrium between 0.0446 M sodium bicarbonate and 0.0173 M sodium carbonate. About 500 mL of solution was used for each scan. All tests were conducted at 40°C, which is a typical storage temperature for the dilute radioactive waste. Air that had been scrubbed of carbon dioxide was bubbled through the solutions during the equilibration period and the CPP scan.

Results

Figure 4 shows the CPP scans obtained from three nitrite-free solutions with the indicated nitrate concentrations, ranging from 0.01 M to 0.3 M. As in all scans the pH was maintained at 9.73 to 9.80 and the test temperature 40 ± 2°C. These scans are typical of those obtained in the test solutions containing either nitrate or chloride as the aggressive ion. At the lowest concentration of nitrate there is seen a wide potential range in which the A537 steel remained in a passive state, with a passive current density relatively constant at a value between 1 and 10 $\mu A/cm^2$. The current density began to increase rapidly with increasing potential (transpassive transition) at a potential of about 0.7 ± 0.1 V vs. SCE. Between 0.01 M and 0.1 M nitrate, a critical concentration of nitrate was reached that induced passive breakdown at potentials < 0.6 volts vs. SCE. (Additional testing will be performed to determine the critical concentration.) In Figure 4 the pitting potential is -0.11 V vs. SCE for 0.1 M nitrate and -0.21 V vs. SCE for 0.3 M nitrate, as determined by the potential of rapid current density increase. Further, at these concentrations a large hysteresis in current density was seen. The current density on the return portion of the scan exceeded that of the forward portion by more than an order of magnitude. Frequently, as Figure 4 shows, the repassivation potential (the potential at which the return scan current density falls below the passive current density) is lower than the original open-circuit potential. The measured open-circuit and pitting potentials in nitrate solutions without nitrite are plotted in Figure 5. Open-circuit potentials are relatively constant over the range of nitrate concentrations tested, ranging from -0.20 V to -0.35 V vs. SCE.

The addition of nitrite at a concentration of 0.11 M to the nitrate solutions has a powerful corrosion-inhibiting action on the CPP scans (Figure 5). Even at a nitrate concentration of 2.2 M, the CPP scan showed transpassive behavior and no evidence of nitrate-induced passive breakdown. The open-circuit potentials tended to increasingly negative values with the higher nitrate levels, but repeated scans continued to show a transpassive transition of about 0.75 V vs. SCE. The higher nitrate concentrations tested did weaken the protectiveness of the passive film: the passive current density increased from about 5 $\mu A/cm^2$ to about 50 $\mu A/cm^2$ with an increase in nitrate from 0.02 to 2.2 M (Figure 7).

The CPP scans performed in chloride solutions at pH 9.73 and 40°C confirm the expectation that chloride is a much more aggressive pitting agent. Open-circuit and pitting potentials without nitrite and with 0.11 M nitrite are plotted in Figures 8 and 9, respectively, as a function of chloride concentration. The open-circuit potentials are similar to those observed in the nitrate solutions, ranging from -0.1 to -0.4 V vs. SCE. There is a tendency again to increasingly negative values with increasing aggressive ion concentration. In the nitrite-free solutions chloride induces passive breakdown at concentrations > 0.001 M, an order of magnitude lower than the comparable nitrate value. With nitrite present at 0.11 M, pitting was initiated at chloride concentrations > 0.01 M, in contrast with the steel's resistance to breakdown in the presence of 2.2 M nitrate. Pitting potentials were not determined for the highest chloride concentrations in Figure 9; the steel specimens freely corroded without achieving passivity. Chloride did not have the effect on the passive current density that nitrate did. In the chloride range 0.0001 to 0.01 M with 0.11 M nitrite present, the passive current density was essentially constant at 5 ± 3 $\mu A/cm^2$ and rose only slightly at the highest tested chloride concentrations.

For halide-induced pitting of metals, the simple relationship between pitting potential E_p and halide ion concentration C_i

$$E_p = A - B*\log C_i$$

has been determined, where A and B are constants.[8] Further data will be acquired to determine accurate constants in the present work. The pitting potentials plotted in Figure 9 for chloride concentrations > 0.01 M do decrease linearly with the logarithm of chloride concentration. The value of the constant B, 0.47 V, falls in the range reported for iron-base alloys.[9]

Conclusions

An electrochemical study has been initiated on pitting corrosion in ASTM A537 carbon steel exposed to dilute alkaline high-level radioactive waste. Nitrate and chloride are known pitting agents in this system, and nitrite is an effective inhibitor of pitting. The effects on the open-circuit and pitting potentials of the two aggressive ions in the presence and absence of nitrite have been measured at a pH of 9.73 (buffered by sodium bicarbonate and sodium carbonate) and a temperature of 40°C. The cyclic potentiodynamic polarization technique was used to measure the potentials. Nitrate was confirmed as a much weaker pitting agent than chloride. In the absence of nitrite, the critical concentration to initiate pitting was 0.01 M for nitrate and 0.001 M for chloride. When 0.11 M nitrite was added to the test solutions, the passive film on the steel did not break down in the nitrate solution (even at 2.2 M) until the transpassive transition (at about 0.75 V vs. SCE). In contrast, chloride concentrations greater than 0.01 M caused pit initiation. The linear equation between the pitting potential and the logarithm of the aggressive ion concentration was demonstrated in the 0.11-nitrite chloride solutions, but additional data are necessary to calculate accurately the constants of the equation.

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Figure 1. Variation of the open-circuit potential of the steel specimen with time for two nitrate concentrations. Nitrite concentration 0.11 M, pH 9.73, temperature 40°C.

Figure 2. Mounted 1.6-cm diameter ASTM A537 class 1 steel specimen.

Figure 3. Four cyclic potentiodynamic polarization scans at 0.02 M nitrate and 0.11 M nitrite.

Figure 4. Cyclic potentiodynamic polarization scans in solutions with indicated nitrate concentrations and no nitrite, showing the onset of pitting with nitrate concentration between 0.1 and 0.3 M.

Figure 5. Variation of open-circuit (OCP) and pitting potentials with nitrate concentration at pH 9.73 and 40°C with no nitrite present.

Figure 6. Variation of open-circuit and pitting potentials with nitrate concentration at pH 9.73 and 40°C with 0.11 M nitrite present.

Figure 7. Variation of passive current density with nitrate concentration in solutions with 0.11 M nitrite present.

Figure 8. Variation of open-circuit and pitting potentials with chloride concentration at pH 9.73 and 40°C with no nitrite present.

Figure 9. Variation of open-circuit and pitting potentials with chloride concentration at pH 9.73 and 40°C with 0.11 M nitrite present.