EFFECT OF TEMPERATURE AND ELECTROLYTE COMPOSITION ON THE SUSCEPTIBILITY OF ALLOY 22 TO LOCALIZED CORROSION

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ABSTRACT

The study of the electrochemical behavior of Alloy 22 has been carried out in various concentrated environments using different sample configurations. Comparisons were made between the electrochemical behaviors of Alloy 22 in concentrated chloride solutions, and in concentrated chloride solutions with nitrate ions (NO$_3^-$). In other experiments, the effect of fluoride ions (F$^-$) was investigated. These comparative studies were performed at various temperatures. The rate of corrosion was found to increase with increase in temperature. The presence of nitrate ions reduced corrosion attack on Alloy 22. F$^-$ was found to be more benign to Alloy 22 compared with chloride ions (Cl$^-$). However, a combination of F$^-$ and Cl$^-$ was found to initiate deeper crevices compared with the only Cl$^-$ in the electrolyte.

INTRODUCTION

This work is in support of the design and performance of high-level nuclear waste containers intended for use for disposal of high-level radioactive waste and spent nuclear fuel in Yucca Mountain, Nevada. On July 23, 2002, The United States Congress approved the site at Yucca Mountain, Nevada, for development as repository for disposal of these materials. Therefore, some of the environmental considerations of importance are those pertaining to the design and performance of high-level radioactive waste packages for the Yucca Mountain Project (YMP). The design of the waste package as stipulated in the License Design Selection Report [1], calls for a double walled container. The proposed material for the outer barrier of the waste package is Alloy 22 (Unified Numbering System (UNS) N06022), the corrosion resistant material (CRM). Alloy 22 is expected to provide a reasonable level of "kinetic" immunity from general and localized corrosion for the waste packages under the prevailing environmental condition in Yucca Mountain. Kinetic immunity would ensure a low rate of passive dissolution, and negligible chance of generating damaging pits or crevices. The proposed material for the inner barrier of the waste package is stainless steel 316NG. The primary role of this layer is structural reinforcement [1].

Extensive studies have been carried out on the effects of temperature (25 to 200 °C) and electrolyte composition (0.017 M chloride concentration ([Cl$^-$]) to saturation) on the critical breakdown potentials for localized corrosion on Nickel (Ni) alloys [2-14]. A decrease in temperature and [Cl$^-$] increases the critical breakdown potential. An increase
in concentration of alloying elements like tungsten (W), chromium (Cr) and molybdenum (Mo) also increases these breakdown potentials. The synergy between Cr and Mo in resisting localized corrosion is particularly effective in raising the breakdown potentials. Alloy 22 is more resistant to localized breakdown, and exhibits much lower corrosion rates compared with alloys such as 625 and 825 [4-6, 11, 15-17]. Consequently, more severe environments are required to initiate breakdown in Alloy 22 compared with Alloys 625 and 825.

In this study, electrochemical tests were performed to determine the effect of temperature on the electrochemical behavior of Alloy 22 in highly concentrated chloride electrolyte, as well as the effect of nitrate ions (NO\textsubscript{3}\textsuperscript{-}), a corrosion inhibiting specie, and the effect of fluoride (F\textsuperscript{-}) on the corrosion resistance. Parameters like the corrosion potential (E\textsubscript{corr}) and the critical breakdown potential (E\textsubscript{crit}) were measured. 5 M CaCl\textsubscript{2} was chosen to represent an extreme bounding condition in pore water concentration. However, it is not expected that concentrated chloride-only solutions (not containing any other anions or oxyanions) will ever be in contact with the surface of the containers in the Yucca Mountain repository [18-20]. Pore water from Yucca Mountain contains a complicated array of species [18-20]. Apart from the fact that this array of species make the water chemistry and the possible specie/metal surface interactions complicated, some of the oxyanions present in the ground water of Yucca Mountain (e.g., nitrate (NO\textsubscript{3}\textsuperscript{-}), sulfate (SO\textsubscript{4}\textsuperscript{2-}) have been found to inhibit localized corrosion in stainless steels and nickel [21-31]. These oxyanions are present in appreciable concentrations [18-20] compared with Cl\textsuperscript{-}, and would be expected to significantly affect the various critical potentials and the onset of localized corrosion on Alloy 22 under service conditions in Yucca Mountain. The addition of NO\textsubscript{3}\textsuperscript{-} to the 5 M CaCl\textsubscript{2} is aimed at investigating the effect of the inhibiting ions in pore water solutions. F\textsuperscript{-} is also contained in the pore water. Thus the addition of F\textsuperscript{-} to the Cl\textsuperscript{-} solution is aimed at understanding what effect the presence of F\textsuperscript{-} will have on the corrosion of the container material. The results presented here highlight the preliminary results of corrosion potential (E\textsubscript{corr}) measurements, as well as slow scan rate potentiodynamic polarization of Alloy 22 in these electrolytes at various temperatures.

**EXPERIMENTAL PROCEDURE**

The material used in this study is Alloy 22. Alloy 22 samples were fabricated from wrought rod and sheet specimens. The chemical composition as documented by the supplier appears in Table 1. The composition is consistent with the ASTM B-574 (for rods) and ASTM-B 575 (for plates/sheets) standards [32, 33]. The rod samples were supplied in the form of 30.48 cm long rods with a diameter of 0.625 cm [34]. The rods were wet ground with 600-grit SiC paper (unless otherwise stated) and rinsed in distilled water before experimentation. A 2.54 cm length of the rod was immersed in the electrolyte in the cell so that the total surface area of the sample immersed was ~5.38 cm\textsuperscript{2}. The rods were used to study the susceptibility of Alloy 22 to pitting corrosion. The other sample configuration was in the form of Multiple Crevice Assembly (MCA) specimens, which look like lollipops [34]. The MCA samples were used in the as-received state after degreasing with acetone and methanol. In the as-received state, the working surfaces of the MCA samples were finished to a root mean square (RMS) roughness factor of between 2 and 4 with an air formed oxide film. The rest of the MCA
consisted of Titanium (Ti) grade 2 nuts, bolts and washers, as well as ceramic crevice formers with multiple ridges. The bolts were Teflon wrapped to prevent these hardware components from being in electrical contact with the specimen. Each crevice former had a total of 12 ridges on it, creating 12 different potential crevice sites on each face of the specimen, and a total of 24 potential sites in each assembly [34]. The assembly was tightened to a torque of 70 in-lb. Teflon tape inserts were placed between the ceramic crevice former and the MCA sample prior to tightening. This was done to fill in the micro voids created by the micro-rough surfaces of the sample and the ceramic crevice former, and to increase the reproducibility of the tight crevices in all samples. The total surface area of the MCA specimen immersed in the electrolyte was 7.43 cm² in some experiments. In other experiments the surface area exposed to electrolyte was 20.58 cm², the difference being in the length of the stem of the sample that was immersed in the solution. These surface area estimates included the area under the 24 ridges of the crevice formers, which had a combined surface area of 1.6 cm². In current density estimations, the surface area of 7.43 or 20.58 cm² was used as appropriate. Therefore, the current density estimates for the MCA samples might be marginally lower than in reality. The MCA samples were used to study the susceptibility of Alloy 22 to crevice corrosion.

A three-electrode cell with a capacity of 1000 cm³ was used for experimentation. The volume of electrolyte in the cell was about 900 cm³. A saturated silver/silver chloride (SSC) (Ag/AgCl) electrode was the reference electrode (RE). The RE was maintained near room temperature by mounting it at the end of a Luggin probe, which had a water-cooled jacket around it. The temperature of the water pumped through the cooling jacket was about 12°C. Thermal liquid junction calculations showed that potential variation caused by this phenomenon was in the order of mV (~10 mV maximum). Also, according to Macdonald et al., a high KCl concentration in the reference electrode tends to suppress thermal liquid junction potentials across the boundary between the high and low temperature solutions [35]. The liquid junction potential variations were therefore ignored in further analyses. The counter electrode was made of platinum (Pt) foil. The temperature of the electrolyte was maintained by means of an oil-filled heating bath. The sample was immersed into the cell after the electrolyte had attained the desired temperature. The temperature was taken before and after the experiment with a thermocouple immersed into the electrolyte. Electrochemical measurements were carried out using a potentiostat. The corrosion potential (Ecorr) was monitored for 24 hours. This was followed by cyclic potentiodynamic polarization measurements immediately afterwards. Cyclic polarization was started approximately 100 mV below Ecorr, and continued until the current density from the sample reached a maximum of up to 30 mAcm⁻², or a maximum of 1.3 V (SSC) before the scan was reversed. The sweep rate in the forward and backward directions was 0.1667 mVsec⁻¹ (600 mVh⁻¹). Deaerated 5 M CaCl₂, 5M CaCl₂ + 0.5 M Ca(NO₃)₂, 1 M NaCl, 1 M NaF and 0.5 M NaCl + 0.5 M NaF were used on the two sample configurations, at various temperatures in these experiments. The pH of 5 M CaCl₂ and 5 M CaCl₂ + 0.5 M Ca(NO₃)₂ was about 6. The pH of 1 M NaCl, 1 M NaF and 0.5 M NaCl + 0.5 M NaF electrolyte were about 7, 9 and 9 respectively. Nitrogen gas (N₂) was bubbled through the electrolytes for at least one hour before and throughout the experiments at a rate of 100 cc/minute. All electrolytes were prepared using certified American Chemical Society (ACS) grade chemicals.
RESULTS AND DISCUSSION

The Effect of Temperature (in 5 M CaCl₂)

The Corrosion Potential (E₉₀₉₉)

Figure 1 shows some examples of 24-hour E₉₀₉₉ transients of Alloy 22 in 5 M CaCl₂ at 60, 75 and 90 °C. The values of the E₉₀₉₉ do not significantly differ between 60 to 90 °C with both rod and MCA samples. The evolution of the E₉₀₉₉ did not follow a particular pattern over this 24-hour period. On some samples the E₉₀₉₉ stayed fairly constant, while on others, it either increased or decreased with time. This pattern was observed irrespective of the temperature. Therefore, these 24-hour E₉₀₉₉ transients are insufficient to predict what trend the evolution of the E₉₀₉₉ of Alloy 22 will follow over longer exposure periods of time. Figure 2 shows the E₉₀₉₉ values for 5 M CaCl₂ plotted as cumulative probability distributions from at least 5 replicates at each test condition. The plotted E₉₀₉₉ values were recorded at the 24-hour mark of the experiments. E₉₀₉₉ decreased with temperature on the rod samples (Figure 2). No such distinct trend was observed with MCA samples. There was more scatter in the values of the E₉₀₉₉ of the rod compared with the MCA samples. The reason(s) for this observation are not clear at this time. Nevertheless, the distributions of the E₉₀₉₉ at various temperatures were very close. There was a difference of approximately 60 mV between the highest and lowest E₉₀₉₉ values at the 50-percentile mark (Figure 2). The values of E₉₀₉₉ for all the samples clustered around -420 mV(SSC).

The Breakdown Potential (E₉₀₉₉₉)

As evident from the polarization curves in Figures 3 and 4 (for rod and MCA samples respectively), and also confirmed by optical microscopy, Alloy 22 is susceptible to localized corrosion in deaerated 5 M CaCl₂ between 60 and 90 °C. No curves were shown for 75 °C because they are essentially similar to those taken at 90 °C. The polarization curves of the rods and MCA are similar except for the fact that the passive current densities for the MCA were higher than that exhibited by the rod samples. The reason(s) for this is not clear. However, one possibility is that there is a more active zone on the edge (non working surface of the sample), which has a slightly different oxide film composition (physical and/or chemical) from that of the working surface. The physical damage to the samples increased with temperature. On the MCA samples, damage was due to crevice attack at all temperatures. On the rod samples, the mode of attack was either by pitting or localized etch-like attack at 60 °C. Localized etch-like attack was the dominant mode of damage at higher temperatures.

E₉₀₉₉ increased as temperature decreased in both sample configurations. At 60 °C, some of the samples experienced a drop in current density after an initial rise in current.

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1 "Critical breakdown potential", E₉₀₉₉₉, as employed here is used to denote the potential(s) at which the breakdown of the passive film occurs by any type of corrosion attack such as pitting corrosion, crevice corrosion, general dissolution, or transpassive dissolution occurs.
density of up to 30 mAcm\(^{-2}\) (Figures 3 and 4). On further increase of potential, the sample eventually proceeded into transpassive dissolution. Examples of polarization curves showing this behavior are shown in Figures 3 and 4 and compared with those in which repassivation did not occur. This behavior did not occur at 75 or at 90 °C. It is not surprising that the critical breakdown potential of Alloy 22 in 5 M CaCl\(_2\) decreased as temperature increased. What was unanticipated was the ability of Alloy 22 to sometimes recover from the high current density excursions (which suggest localized breakdown) at 60 °C (Figures 3 and 4).

Figures 5 and 6 show \(E_{\text{crit}}\), and the \(E_{\text{corr}}\) of the rod and MCA samples respectively as a function of potential at 60, 75 and 90 °C plotted as cumulative probabilities. Two methods were used to estimate \(E_{\text{crit}}\). In the first method (Method 1), \(E_{\text{crit}}\) was the potential at which the threshold current density [signified by the vertical line in Figures 3 and 4] of \(2 \times 10^{-5}\) Acm\(^{-2}\) (20 \(\mu\)Acm\(^{-2}\))\(^2\) was attained. As seen from Figures 3 and 4, Method 1 did not take into account the decrease in current density in the “hump” of the curves of both the rod and MCA samples at 60 °C, nor the fact that the current density in the passive region of the MCA samples were generally above the threshold current density. In the second method (Method 2), \(E_{\text{crit}}\) was taken as the potential that coincided with the onset of the first permanent rise in current density from the passive region. An asterisk (*) is used to denote the \(E_{\text{crit}}\) values obtained by Method 2. For rod samples (Figure 5), only the data from the 60 °C measurements by Method 2 are plotted. The differences observed between the \(E_{\text{crit}}\) values measured by Methods 1 and 2 at 75 and 90 °C were not as significant as those observed at 60 °C. For the MCA samples (Figure 6), data from both measurement methods are presented at all temperatures.

The \(E_{\text{crit}}\) due to pitting and localized etch-like breakdown (rod samples) were much higher than those due to crevice attack obtained from the MCA samples (Figures 5 and 6). The difference between the highest \(E_{\text{corr}}\) and the lowest \(E_{\text{crit}}\) obtained on the rod samples was about 300 mV (Figure 5). With the MCA samples, the difference between highest \(E_{\text{corr}}\) and the lowest \(E_{\text{crit}}\) when measured by Method 1 was about 25 mV, and about 200 mV measured by Method 2. It should be noted that at 60 °C the \(E_{\text{crit}}\) values for both the rods and MCA due to localized breakdown were not separated from those due to transpassive dissolution. The higher \(E_{\text{crit}}\) exhibited by the rod samples compared with the MCA samples shows that it is more difficult to initiate and propagate localized corrosion on an open surface of Alloy 22 compared with an occluded surface even at very high chloride concentrations. This clearly indicates that crevice corrosion is much more of a threat (more easily initiated) to Alloy 22 than pitting corrosion. At the 50-percentile probability mark (Figure 5 and 6), the rods had a critical breakdown potential of about 170, 105 and 20 mV at 60, 75 and 90 °C respectively, while the MCA samples had a critical potential of about -280 mV at all the three temperatures (using Method 1). At 60 °C, the \(E_{\text{crit}}\) of the rod samples was lower than that of the MCA samples (at 50-percentile probability mark breakdown occurs at, ~500 and ~700 mV respectively) when measured by Method 2. A possible reason for why the onset of transpassive passive dissolution occurs at a lower potential on the rod compared to the MCA samples is probably because the presence of the ceramic former on the MCA samples acted as a barrier to diffusion of species during transpassive dissolution.

\(^2\) At this current density, stable pitting or crevice corrosion would usually have commenced for various stainless steels, nickel and Alloy 22 [4, 5, 36, 37].
Under the environmental conditions in Yucca Mountain, it is unlikely that waste containers fabricated from Alloy 22 will ever be in contact with solutions of a chloride-only composition. For this reason, 5 M CaCl₂ (10 M Cl⁻) must be regarded as a theoretical extreme bounding environment with little possibility of its presence without any other anions or oxyanions being present under real-life repository conditions. Earlier work showed that Alloy 22 is not susceptible to localized corrosion in simulated concentrated solutions that are relevant to the repository ground water [20].

The Effect of Nitrate

The E_{corr} of Alloy 22 MCA samples at 90 °C in 5 M CaCl₂ + 0.5 M Ca(NO₃)₂ was about -300 mV. This was about 120 mV higher than the average value for Alloy 22 MCA samples in 5 M CaCl₂. Figure 7 shows the cyclic polarization curves of Alloy 22 MCA samples at 90 °C in 5 M CaCl₂ and in 5 M CaCl₂ + 0.5 M Ca(NO₃)₂. One of the effects of addition of nitrate is the appearance of a prominent active-passive peak (with current densities in excess of 10⁻⁴ A cm⁻²), which is not present in the Cl⁻ only electrolyte at 90 °C. From Figure 7 it is apparent that adding nitrate to the 5 M CaCl₂ caused E_{crit} to increase. This increase was about 76 mV if estimated using Method 1. However, if the threshold current density (20 μA cm⁻²) was imposed after the active-passive loop/transition on the 5M CaCl₂ + 0.5M Ca(NO₃)₂ curves, the increase in critical potential for breakdown was about 267 mV. Examination of the tested samples showed that Alloy 22 had considerably less localized corrosion attack in 5 M CaCl₂ + 0.5 M Ca(NO₃)₂ solutions at 90 °C compared with 5 M CaCl₂. The area and depth of attack in the presence of NO₃⁻ was much less, than in its absence. These results show a clear inhibiting effect of nitrate (NO₃⁻) to localized corrosion on Alloy 22 at high chloride concentrations.

The Effect of Fluoride

The corrosion potential (E_{corr}) (determined from two repeats) for Alloy 22 MCA samples in 1 M NaF, 1 M NaCl and 0.5 M NaF + 0.5 M NaCl at 90 °C were about -660, -450 and -480 mV respectively. Figure 8 shows representative polarization curves of MCA Alloy 22 samples in 1 M NaF, 1 M NaCl and 0.5 M NaF + 0.5 M NaCl at 90 °C. In this figure, the lowest passive current density for Alloy 22 is exhibited in 1 M NaF followed by 0.5 M NaF + 0.5 M NaCl, and then in 1 M NaCl. The difference in passive current density between the Cl⁻ and F⁻ only systems is about two decades. Alloy 22 exhibited two short passive regions in 0.5 M NaF + 0.5 M NaCl. Apart from these two passive regions, the current density increased steadily in the anodic region of the curves. Alloy 22 was susceptible to crevice corrosion in all three environments albeit to varying degrees. The lowest E_{crit} (using Method 1) on Alloy 22 was observed in 1 M NaCl, followed by that in 1 M NaF, and then 0.5 M NaF + 0.5 M NaCl. The average values were about -316, 275 and 283 mV(SSC) respectively. These are the average values from two repeats. Visual inspection of the MCA samples under an optical microscope showed that the amount of physical damage due to dissolution was minimal in all the systems compared with that sustained in 5 M CaCl₂. Damage per unit area was least in 1 M NaF and severest in 1 M NaCl. However, the depth of attack was most severe in 0.5 M NaF +
0.5 M NaCl even though there was less surface per unit area damaged by crevice corrosion.

**CONCLUSIONS**

1) Alloy 22 is susceptible to localized corrosion in 5 M CaCl₂ to temperatures as low as 60 °C.

2) The onset of localized corrosion is shifted to higher potentials as temperature decreased.

3) Alloy 22 exhibited an anodic peak or “hump” at between 200 and 300 mV at 60 °C. This was not observed at 75 and 90 °C.

4) Localized corrosion was inhibited on Alloy 22 at 90°C in an electrolyte consisting of a 10:1 molar ratio of Cl⁻ to NO₃⁻ (5 M CaCl₂ + 0.5 M Ca(NO₃)₂).

5) Alloy 22 was susceptible to localized corrosion in 1 M NaCl, 1 M NaF and 0.5 M NaCl + 0.5 M NaF at 90 °C. Corrosion damage was least in 1 M NaF. The deepest damage occurred in 0.5 M NaCl + 0.5 M NaF, and the most extensive damage by surface area occurred in 1 M NaCl.

**REFERENCES**

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