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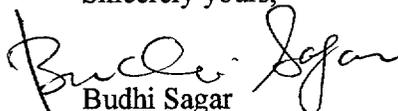
Subject: Programmatic review of Materials Research Society 24<sup>th</sup> International Symposium on the Scientific Basis for Nuclear Waste Management paper titled "Corrosion Processes Affecting the Performance of Alloy 22 as a High-Level Radioactive Waste Container Material"

Dear Mrs. DeMarco:

Attached is the paper to be presented at the Material Research Society (MRS) 24<sup>th</sup> International Symposium on the Scientific Basis for Nuclear Waste Management to be held on August 27–31, 2000 in Sydney, Australia. The paper is focused on the performance of Alloy 22 as a high-level nuclear waste container material. Experimental results from passive corrosion, localized crevice corrosion, and stress corrosion cracking tests, conducted in a range of simulated near-field repository environments will be presented, as well as the theoretical modeling of the long-term passive corrosion behavior. The paper after being reviewed and approved by the Conference Chairs will be published in the Proceedings of the Symposium by the Materials Research Society.

Please contact Gustavo Cragolino at (210) 522-5539 if you have any questions regarding this paper.

Sincerely yours,



Budhi Sagar  
Technical Director

BS:GC:jg

Enclosure

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## **CORROSION PROCESSES AFFECTING THE PERFORMANCE OF ALLOY 22 AS A HIGH-LEVEL RADIOACTIVE WASTE CONTAINER MATERIAL**

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### **ABSTRACT**

Alloy 22 is the material preferred by the U.S. Department of Energy (DOE) for the waste package (WP) outer container for geological disposal of high-level radioactive waste at the proposed site in Yucca Mountain (YM). Alloy 22 is considered to be extremely resistant to various modes of aqueous corrosion over broad ranges of temperature, pH, and concentration of anionic and oxidizing species. Uniform corrosion under passive dissolution conditions, localized corrosion in the form of crevice corrosion, and stress corrosion cracking (SCC) are discussed on the basis of experimental results obtained with mill annealed, thermally treated, and welded specimens using electrochemical techniques. The approach developed for long-term performance prediction, including the use of empirically derived parameters for assessing localized corrosion and the modeling of the passive dissolution behavior, is described.

### **INTRODUCTION**

One of the principal factors in the DOE Repository Safety Strategy for the proposed repository at YM [1] is the performance of the WP barriers. It is expected that the integrity of the WPs, predicated on the use of a highly corrosion-resistant alloy as an outer container material, will prevent exposure of the radioactive waste (spent nuclear fuel and vitrified reprocessed waste) to the environment for times longer than the regulatory performance period of 10,000 yr. During this period, the environment in contact with the WPs, initially dry hot-air, may become an aggressive aqueous solution as a result of dripping of groundwater, altered in its chemical composition by interactions with the host rock and evaporative concentration due to radioactive decay heating. The currently proposed DOE WP design consists of a 2-cm thick alloy 22 (57Ni-22Cr-13.5Mo-3W-3Fe) outer container enclosing a 5-cm thick inner container made of type 316 nuclear grade (NG) stainless steel. The main purpose of the inner container is to provide structural integrity to the WP. Alloy 22 became the material preferred by the DOE for the outer container because it is more resistant to localized corrosion in the predicted WP environment than other Ni-Cr-Mo alloys previously considered, such as alloys 825 and 625 [2, 3].

The objective of this paper is to provide a summary of the results of our experimental investigations on the various corrosion processes (passive corrosion, crevice corrosion, and SCC) that are expected to affect the long-term performance of the alloy 22 containers in the repository. Information previously reported [4, 5] is updated with new results and the modeling of long-term passive dissolution [6] is briefly described.

### **EXPERIMENTAL**

The chemical composition of the two heats of Alloy 22 used in this study, as well as the composition of the filler rod used for welded specimens, and the geometry and dimensions of the specimens used in the various tests were reported elsewhere [4, 5]. Smooth cylindrical specimens were used in potentiostatic tests to measure the passive dissolution current density. Specimens with a metal/PTFE

crevice were used in cyclic potentiodynamic polarization (CPP) tests to measure the repassivation potential for crevice corrosion ( $E_{\text{rrev}}$ ). Mill annealed (MA), thermally treated (TT) (at 870 °C for times ranging from 0.5 to 240 hr), and welded (W) specimens were employed in the potentiostatic and CPP tests. Fatigue precracked double cantilever beam (DCB) specimens, manufactured from MA plates, were adopted for the SCC tests.

Passive dissolution current density measurements were conducted at 20 and 95 °C in  $N_2$ -deaerated 0.028 to 4.0 M NaCl solutions at various pHs. CPP tests were carried out in an autoclave system using solutions containing 0.5 to 4.0 M  $Cl^-$ , 1.24 mM  $HCO_3^-$ , 0.20 mM  $SO_4^{2-}$ , 0.16 mM  $NO_3^-$ , and 0.10 mM  $F^-$ , added as sodium salts, at temperatures ranging from 80 to 175 °C. SCC tests were conducted in solutions containing 5 wt % NaCl (0.9 molal  $Cl^-$ ) at 90 °C and 40 wt %  $MgCl_2$  (14.0 molal  $Cl^-$ ) at 110 °C under open circuit (OC) conditions. The 5 wt % NaCl solution was acidified to pH 2.7 by the addition of HCl and purged with  $N_2$  to reproduce the conditions reported by Roy et al. [7]. Additional experimental details have been reported elsewhere [4, 5].

## RESULTS

**Passive Corrosion** — As noted previously [4], alloy 22 exhibits passive behavior over a potential range of about 800 mV that extends from the corrosion potential ( $E_{\text{corr}}$ ) in deaerated solutions ( $\sim -600$  mV<sub>SCE</sub>) to the potential for transpassive dissolution. Steady-state anodic current densities for the dissolution of MA alloy 22, measured potentiostatically for various  $Cl^-$  concentrations and pHs at 95 °C, are plotted in Figure 1 as a function of the applied potential. Passive corrosion was observed up to potentials of approximately 400 mV<sub>SCE</sub>, as indicated by current densities lower than  $10^{-7}$  A/cm<sup>2</sup>, which are almost independent of potential,  $Cl^-$  concentration and pH. The passive current density was not affected by decreasing the temperature from 95 to 20 °C, with the exception of the most diluted chloride solution (0.028 M) in which a decrease of about 10 times was measured at 200 mV<sub>SCE</sub> (Figure 2). Transpassive dissolution was observed at potentials just above 400 mV<sub>SCE</sub> in the acidic solutions at 95 °C but occurred at slightly higher potentials with increasing pH (Figure 1) or decreasing temperature (Figure 2). At pH 8, transpassive dissolution was accompanied by the onset of the oxygen evolution reaction. No evidence of localized corrosion was detected for the MA, non-creviced specimens in these potentiostatic tests ( $\sim 48$  hr duration) over the potential range of  $-200$  to 800 mV<sub>SCE</sub>.

As reported previously [5], TT (4 and 24 hr at 870 °C) alloy 22 also exhibited passive corrosion in 4 M NaCl (pH 8) solutions at 95 °C. However, significant intergranular attack was observed in some potentiostatic tests at potentials as low as 0 mV<sub>SCE</sub> and more consistently at 200 mV<sub>SCE</sub> and above. The W specimens, in which the weld extended over one-fourth of the total exposed surface area (20 cm<sup>2</sup>), exhibited a passive current density ranging from  $2.0 \times 10^{-8}$  to  $4.0 \times 10^{-8}$  A/cm<sup>2</sup> at potentials lower than 400 mV<sub>SCE</sub> in 4 M NaCl solutions at 95 °C [5]. Even though the current density was found to be slightly higher in the acidic solutions, it was practically independent of pH in the range of 2.7 to 11. However, the current density increased significantly at 600 mV<sub>SCE</sub> for both pH 2.7 and 11 solutions and at higher potentials for the pH 8 solution indicating the occurrence of transpassive dissolution. Although preferential dissolution of the weld region, revealing its microstructure, was noted, no intergranular corrosion of the adjacent base metal was observed [5].

**Localized corrosion** — As discussed previously [3], alloy 22 is susceptible to localized corrosion in the form of crevice corrosion within certain ranges of  $Cl^-$  concentration and temperature as other Ni-Cr-Mo alloys (825 and 625). However, the minimum  $Cl^-$  concentration and the potential required for crevice corrosion to be initiated at a given temperature (e.g., 95 °C) are both higher for alloy 22 than for the other alloys. A plot of  $E_{\text{rrev}}$  for MA alloy 22 as a function of temperature is shown in Figure 3, in which a

significant decrease in the  $E_{\text{rcrev}}$  values (allowing for a data scattering of  $\pm 100$  mV) can be observed for the three  $\text{Cl}^-$  concentrations with an increase in temperature from 80 to 105 °C, followed by a leveling off at higher temperatures. When the  $E_{\text{rcrev}}$  values (using only those that represent a low bound) are replotted as a function of the logarithm of the  $\text{Cl}^-$  concentration (Figure 4), a linear dependence is satisfied up to 150 °C, according to the following expression

$$E_{\text{rcrev}} = E_{\text{rcrev}}^0(T) + B(T) \log [\text{Cl}^-] \quad (1)$$

where both  $E_{\text{rcrev}}^0$  and  $B$  are parameters that, within the 80 to 105 °C temperature range, can be expressed through a data regression (note that coefficients are changed with respect to those in Ref [4]) as Eq. [2]

$$E_{\text{rcrev}}^0(T) = 1,300 - 13.1 T ; B(T) = -362.7 + 2.3 T \quad (2)$$

where  $T$  is the temperature in °C and  $E_{\text{rcrev}}$  is in  $\text{mV}_{\text{SCE}}$ . It is apparent from Eq. (2) that  $E_{\text{rcrev}}$  is strongly dependent on temperature around the boiling point of water at atmospheric pressure and the dependence on  $\text{Cl}^-$  concentration decreases with increasing temperature.

As noted before [5], TT (only for 0.5 hr at 870 °C) alloy 22 exhibited a decrease in  $E_{\text{rcrev}}$  of more than 500 mV in 4 M NaCl solution at 95 °C, promoted by the occurrence of intergranular corrosion in the crevice region of the specimen. However, when W specimens are compared to MA specimens, as shown in Figure 5, the effect of welding on  $E_{\text{rcrev}}$  appears to be negligible at both 95 and 125 °C.

**Stress corrosion cracking** — The SCC susceptibility of MA alloy 22 was investigated in  $\text{Cl}^-$  solutions using the test conditions given in Table 1. Tests were conducted at an initial stress intensity ( $K_I$ ) equal to  $32.7 \text{ MPa}\cdot\text{m}^{1/2}$ . No crack growth was observed in any of the fatigue precracked DCB specimens over the duration of the tests. Periodic SEM examination of the specimens (approximately 1-month intervals) revealed that grain boundary attack occurred after 147 d of testing in the 22-2 (T-L) specimen and minor secondary cracking near the main precrack in the 22-7 (S-L) specimen after 70 d. However, the secondary cracks did not propagate during the subsequent exposure to the environment for the entire duration of the test. Assuming that the initiation time is negligible and  $20 \mu\text{m}$  is the smallest crack detectable in the SEM, the minimum crack velocity that can be measured over the test period listed in Table 1 would be  $\sim 6.0 \times 10^{-13}$  m/s. In the case of type 316 L stainless steel, although crack growth was not observed in the pH 2.7 NaCl solution at 90 °C, crack propagation rates of about  $1 \times 10^{-8}$  m/s were measured at

**Table 1— Test conditions and results for the SCC testing of Alloy 22 DCB specimens**

Specimen ID (Orientation)	Test Solution and Temperature	Potential ( $\text{mV}_{\text{SCE}}$ )	Duration (hr)	Result
22-1(T-L)	0.9 molal $\text{Cl}^-$ (5% NaCl), pH 2.7 90°C, $\text{N}_2$ deaerated	-330 to -310 (OC)	9,264 (386 days)	No SCC
22-2(T-L)	14.0 molal $\text{Cl}^-$ (40% $\text{MgCl}_2$ ), 110°C	-280 to -260 (OC)	9,264 (386 days)	No SCC – Grain Boundary Attack
22-7(S-L)	14.0 molal $\text{Cl}^-$ (40% $\text{MgCl}_2$ ), 110°C	-270 to -250 (OC)	9,264 (386 days)	No SCC –Secondary Cracking

T-L – Transverse-Longitudinal; S-L – Short transverse-Longitudinal; OC – Open-Circuit

the OC potential ( $-330$  to  $-320$  mV<sub>SCE</sub>) in a 9.1 molal Cl<sup>-</sup> (30 % MgCl<sub>2</sub>) solution at 110 °C [8]. Nevertheless, even for precracked specimens under a constant, applied load the initiation time appears to be significant (hundreds of hours) based on our current on-going work

## DISCUSSION AND CONCLUSIONS

If localized corrosion is not initiated and the  $E_{\text{corr}}$  of the container is lower than 400 mV<sub>SCE</sub>, the lifetime of an alloy 22 WP container can be predicted from the potentiostatic measurements of the passive current density and the application of Faraday's laws [4]. By assuming congruent dissolution of the alloy constituents and a passive current density of  $3.0 \pm 0.5 \times 10^{-8}$  A/cm<sup>2</sup> (see Figure 1), the lifetime of a 2-cm thick container may extend from ~58,000 to ~82,000 yr. However, there are uncertainties in the long-term extrapolation of passive corrosion and mechanistic modeling of passivity is necessary to define conditions for additional experimental studies and more reliable performance assessments.

As for other Ni-Cr alloys in which the Cr content is greater than 12 to 15 wt%, the passive dissolution rate of alloy 22 is low as a result of the formation of a protective Cr<sub>2</sub>O<sub>3</sub>-rich film on the metal surface [9]. A model for the passive dissolution of Ni-Cr-Mo alloys, based on the point defect model (PDM) [10], is being developed [6]. It is assumed that the conduction mechanism through the Cr<sub>2</sub>O<sub>3</sub> film formed on these alloys is mainly by interstitial cations or oxygen vacancies or by both carriers, which implies a steady-state passive current density independent of potential (see Figure 1). Cation vacancies are the carriers in the NiO film on pure Ni [10], which exhibits a passive current density that increases exponentially with potential [11]. It is assumed in the model that the Cr<sub>2</sub>O<sub>3</sub> film, lacking relevant proportions of Mo, contains Cr, Ni, and Mo as interstitial defects, Ni as a substitutional defect, and oxygen and Cr vacancies. Based on the observation that the passive current density decreases with increasing Cr content in Ni-Cr alloys, it can be demonstrated that preferential dissolution of Ni occurs through the Cr-rich passive film, as reported by Cavanaugh et al. [12]. As a result of constraints in the assumed values of the rate constants for the elementary reactions associated with the creation of interstitials (Cr, Ni, and Mo) and substitutionals (Cr and Ni) at the metal/film interface, charge transport through the passive film is mainly due to interstitial species and, thus, vacancies are created in the bulk of the alloy.

The evolution of the alloy sample thickness as a result of passive dissolution and the vacancy volume in the bulk of the alloy can be estimated, by assuming that the atomic volume of the alloy is constant regardless of the compositional change with time. Figure 6 presents an example of this calculation for three cases in which different values have been assumed for the elementary rate constants, in addition to the initial ( $t=0$ ) passive dissolution current density for alloy 22. With the assumption that a void volume/total volume ratio of 0.5 would lead to failure of the container wall, a lifetime of about 30,000 yr was calculated as shown in Figure 6, even though the wall thickness did not diminish significantly. More refined computations, taking into account vacancy diffusivity in the bulk of the alloy, indicate that vacancies tend to accumulate at the metal/film interface, which may lead to spalling of the passive film. Lifetimes of ~10,000 yr have been computed by assuming that film spalling occurs when a critical vacancy concentration of about 20 % is reached at the metal/film interface.

An even significantly shorter container life is predicted if localized corrosion occurs. Pitting corrosion of alloy 22 was not observed and crevice corrosion may occur only above 80 °C when the Cl<sup>-</sup> concentration is equal or greater than 1.0 M and  $E_{\text{corr}}$  is higher than  $E_{\text{rcrev}}$ . Within the temperature range of 80 to 105 °C,  $E_{\text{rcrev}}$  exhibited a linear dependence on temperature and on the logarithm of Cl<sup>-</sup> concentration, similar to that found for other Ni-Cr-Mo alloys [2]. The  $E_{\text{rcrev}}$  values calculated by using Eq. (2) can be used as a lower bound for assessing the susceptibility to crevice corrosion of the alloy. However, material thermally treated within the temperature/time domain in which TCP phases can precipitate [5],

exhibited significantly lower  $E_{\text{rrev}}$  values. The range of passivity is therefore reduced by the occurrence of crevice corrosion. Also, under certain fabrication conditions (e.g., slow cooling of thick sections) intergranular corrosion may occur at potentials within the passive range.

SCC is a very insidious failure mode in many applications. However, no crack growth of MA alloy 22 has been observed in this study even in extremely concentrated, acidic and hot  $\text{Cl}^-$  solutions, such as 40 %  $\text{MgCl}_2$  at 110 °C. It appears that the  $E_{\text{corr}}$  in these OC potential tests is lower than  $E_{\text{rrev}}$  and thus, crack initiation does not occur regardless of the use of precracked DCB specimens stressed at a relatively high  $K_I$ . Nevertheless, additional tests, including W specimens, are needed to evaluate the effect of higher potentials or dissolved species present in the WP environment and able to induce crack initiation and growth.

## ACKNOWLEDGMENT

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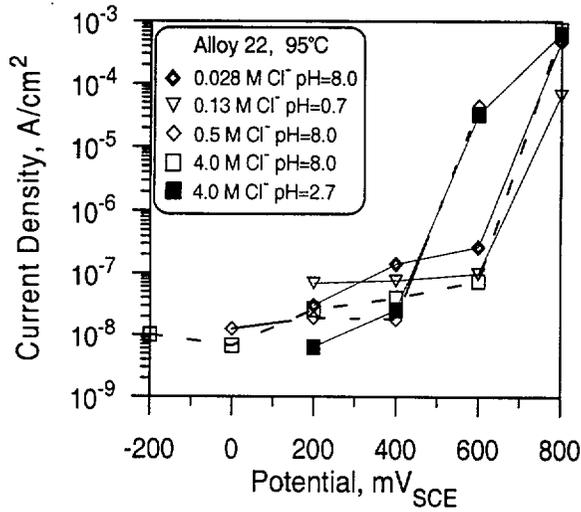


Figure 1. Steady-state anodic current densities for Alloy 22 in Cl<sup>-</sup> solutions at 95 °C.

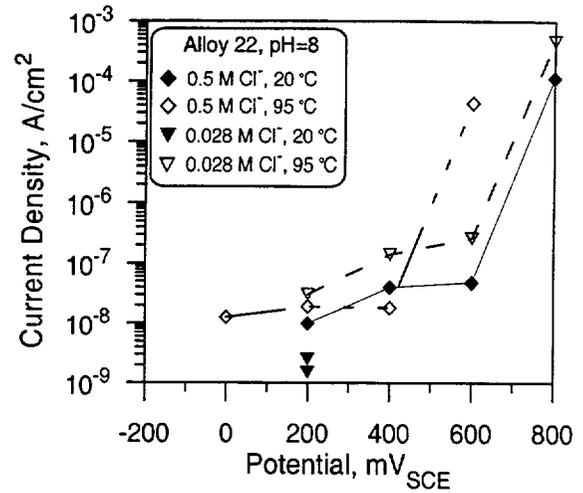


Figure 2. Effect of temperature on steady-state anodic current densities for Alloy 22.

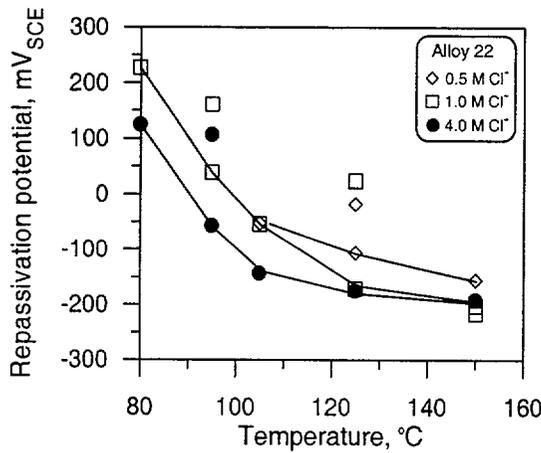


Figure 3. Effect of temperature on the repassivation potential for crevice corrosion of Alloy 22 in Cl<sup>-</sup> solutions.

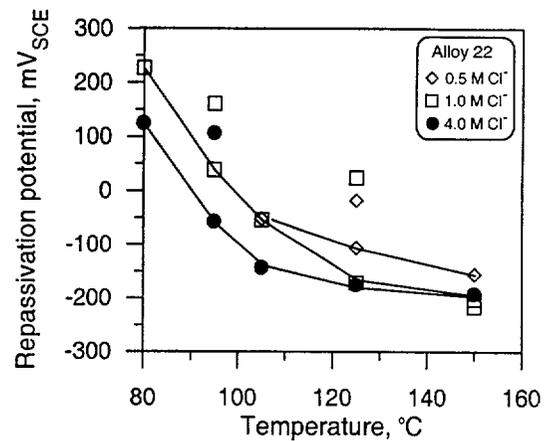


Figure 4. Repassivation potential as a function of Cl<sup>-</sup> concentration for crevice corrosion of Alloy 22 at various temperatures.

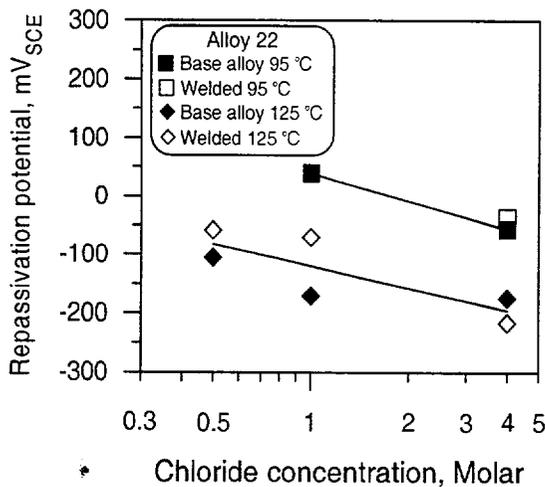


Figure 5. Repassivation potential for crevice corrosion for Alloy 22 in Cl<sup>-</sup> solutions.

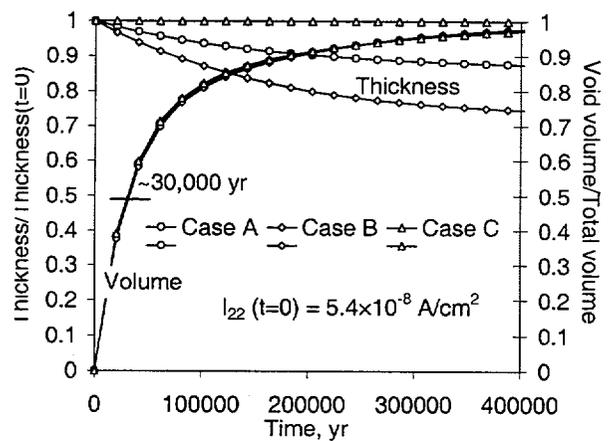


Figure 6. Wall thickness and void volume fraction for three cases with different rate constants for the elementary processes at metal/film interface.