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A. K. Roy
D. L. Fleming
B. Y. Lim

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Lawrence
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National
Laboratory

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Initiation and Growth of Localized Attack in Nuclear Waste Package Materials

Ajit K. Roy
Framatome Cogema Fuels
c/o LLNL (On Assignment)
P.O.Box 808, M/S L-369
Livermore, CA 94551

Dennis L. Fleming
Beverly Y. Lum
Lawrence Livermore
National Laboratory
P.O.Box 808
Livermore, CA 94551

Abstract

Electrochemical potentiodynamic and potentiostatic polarization experiments were conducted on several candidate nuclear waste package container materials in an acidic brine containing 5 weight percent (wt%) NaCl at various temperatures. Substantial pitting and crevice corrosion was observed in Alloys 825 and G-3 in a 90°C brine at controlled potentials (E_{cont}) that were noble compared to the critical pitting potential (E_{pit}) measured by the potentiodynamic polarization method in a similar environment. The results of potentiostatic polarization experiments performed in a 30°C brine at E_{cont} values that were noble compared to the corrosion potential (E_{corr}) indicate that Alloys 825, G-30, C-4 and 625 suffered from crevice corrosion. Alloy C-22 became susceptible to crevice corrosion at 60°C under controlled potentials which were sufficiently noble compared to E_{corr}, suggesting that it had a higher critical crevice corrosion temperature compared to that of the other high-nickel alloys tested. No pitting was observed at 30°C and 60°C on any tested materials. But Alloy 625 showed surface cracks in the crevice region. Ti Grade-12 was immune to localized attack. Tests are ongoing.

Introduction

Electrochemical cyclic potentiodynamic polarization (CPP) experiments have been performed at the Lawrence Livermore National Laboratory (LLNL) on several candidate nuclear waste package container materials to evaluate their susceptibility to localized attack such as pitting and crevice corrosion in environments relevant to the potential underground Yucca Mountain repository. The recent results(1) indicate that iron-nickel-chromium-molybdenum (Fe-Ni-Cr-Mo) Alloys 825, G-3 and G-30 underwent pitting and crevice corrosion in all tested environments, with Alloy 825 showing the worst performance. These results also showed that Ni-Cr-Mo Alloy C-22, and a titanium alloy Ti Grade-12 were immune to localized attack in similar environments. More recently, Alloy 625, also a Ni-Cr-Mo alloy, was tested in order to compare its localized corrosion resistance to that of Alloy C-22. It showed surface degradation(2) including crevice corrosion, pitting corrosion, and cracking. In view of these test results, longer-term potentiodynamic and potentiostatic polarization experiments were performed to evaluate the initiation and growth of localized corrosion in susceptible alloys, the results of which are presented in this paper.

Materials and Environments

Materials tested include Alloys 825, G-3, G-30, C-4, 625, C-22, and Ti Grade-12. Their chemical compositions are given in Table 1. Test specimens were fabricated from solution-annealed materials by a qualified outside vendor, and were tested without any additional thermal treatments. Tests were conducted in an acidic brine containing 5 wt% NaCl at 30°C, 60°C and 90°C. The selection of an acidic brine as test environment is based on previous results(1) which showed the maximum susceptibility of a few candidate alloys to localized attack in a similar environment.

Experimental Procedure

The experimental details of CPP technique have been given elsewhere(1,2), and therefore, will not be repeated. The E_{corr} value for each material was measured followed by the determination of E_{pit} and the protection potential (E_{prot}) values, if available from the CPP diagram. An electrochemical potential scan rate of 0.17 mV/sec was used in this study. The E_{pit} value measured by CPP was used to select the E_{cont} value ($E_{cont} > E_{pit}$) in the potentiostatic polarization experiments performed during the initial phase of this testing program using disc-shaped specimens. Later, potentiostatic experiments were conducted using cylindrical specimens at E_{cont} value which was more noble compared to E_{corr} value ($E_{cont} > E_{corr}$) of materials of interest in a specific environment.

More recently, the test specimen has been polarized at potential scan rates of 10^{-6} and 0.17 mV/sec under potentiodynamic control until a change in slope is observed in the potential versus current density (E vs I) curve. The critical potential at which the slope-change occurred was recorded followed by continued polarization of the specimen at this potential under potentiostatic control for an extended period. This technique is thought to provide information as to the crevice/pitting initiation time, and the extent of localized damage to the specimen over a desired test duration. A limited number of tests using this approach have been completed at the time of writing of this paper, the results of which will also be included in the next section.

The pH of the test solution was measured at room temperature prior to initiation of each experiment. At the conclusion of each test, the specimen was cleaned with distilled water and ethanol. The cleaned specimen was visually examined, followed by an optical microscopic evaluation to detect the mode and extent of degradation.

Results and Discussion

Tests at $E_{cont} > E_{pit}$

Controlled potentials of 150, 160, 170 and 180 mV (versus Ag/AgCl) were selected for tests involving Alloy 825 in view of its measured E_{pit} value of 130 mV in an acidic brine of 5 wt% NaCl at 90°C. Results indicate that pitting was initiated at all E_{cont} values, the extent of pitting being more pronounced at higher applied potentials, as shown in Figure 1. Except at 150 mV, fairly deep round pits were observed in specimens tested at the other three E_{cont} values. These three specimens were also characterized by deep crevice corrosion which possibly resulted from solution trapped under the gasket used in the specimen holder. Most of the pits were located away from the crevice region.

For Alloy G-3, tests were performed in a similar environment at E_{cont} values of 355, 390, 420 and 440 mV since an E_{pit} value of 326 mV (Ag/AgCl) was obtained from the CPP diagram. Pitting was observed at all four E_{cont} values. However, their shapes were different from those seen on Alloy 825 specimens. In contrast to round pits observed with Alloy 825, pits observed in Alloy G-3 specimens were elongated and deeper, with some pits being located along the crevice boundary. As observed with Alloy 825, the maximum pitting of Alloy G-3 was experienced at the highest applied potential

Tests at $E_{cont} > E_{corr}$

The measured E_{corr} value for Alloy 825 in 30°C brine ranged between -164 and -285 mV. Potentials of 250, 275, 300 and 350 mV with respect to E_{corr} value were used under potentiostatic control to initiate localized attack in this alloy. Results indicate that this material was immune to pitting/crevice corrosion at E_{cont} values of 250 and 275 mV for exposure time of 125 and 90 hours, respectively. Severe crevice corrosion was observed with this alloy at the higher E_{cont} values even after exposure for only 20 hours. For Alloy G-30, no localized attack was observed in a similar environment at E_{cont} values of 200-300 mV, but it became susceptible to crevice corrosion at 350 and 400 mV after 20 hours of testing at 30°C. Similarly, Alloy C-4 did not show any attack at E_{cont} values of 200 and 300 mV at 30°C. However, crevice corrosion was observed in this alloy at an applied potential of 350 mV at this temperature.

As to the localized corrosion behavior of Alloys 625 and C-22, the former alloy exhibited tendency to crevice corrosion in 30°C brine at E_{cont} values of 650, 750 and 800 mV after testing for 167 hours. Furthermore, surface cracks were observed with this material in the crevice region. On the other hand, Alloy C-22 was immune to localized attack in the same environment at potentiostatic potentials of 500, 600 and 700 mV for a similar test duration. However, this alloy experienced crevice corrosion tendency at 60°C under an E_{cont} value of 700 mV, suggesting that the critical crevice corrosion temperature for Alloy C-22 may be higher than that for Alloy 625 when tested in an acidic brine under potentiostatic control. No pitting was observed with any high-nickel alloys tested at 30°C and 60°C. Finally, Ti Grade-12 was immune to localized corrosion at E_{cont} values of 500-750 mV even up to a test temperature of 90°C.

Combined Potentiodynamic and Potentiostatic Tests

For Alloy C-22, the results of a room temperature potentiodynamic polarization experiment performed at a potential scan rate of 10^{-6} mV/sec indicated a slope change in the E vs I curve at an approximate electrochemical potential of 810 mV. The test specimen was then potentiostatically polarized for almost 96 hours at an E_{cont} value of 820 mV. The specimen did not exhibit any localized attack; only slight discoloration of the specimen was noticed.

A second potentiodynamic test was performed in a similar environment using an Alloy C-22 specimen at a potential scan rate of 0.17 mV/sec, that showed a slope change in the polarization diagram at around 864 mV. An examination of the same specimen, which was subsequently polarized under potentiostatic control at 870 mV for almost 94 hours, revealed more discoloration of the test specimen yet no localized corrosion. The potentiostatic polarization diagram, as illustrated in Figure 2, showed gradual increase in current density up to 33 hours of testing, followed by a sharp drop between 33 and 50 hours, and eventual stabilization beyond this period.

The result of an ambient temperature potentiostatic polarization experiment involving Alloy 625 in a similar environment at an E_{cont} value of 854 mV is shown in Figure 3. A drop in current density was observed in the E vs I curve up to the initial 9 hours of testing, followed by a gradual shift in the upward direction until reaching a stable value after 50 hours of testing. An examination of the polarized specimen by optical microscopy showed both crevice corrosion and surface attack in and around the crevice region, but no pits. Additional potentiostatic testing for much longer duration is in progress using both Alloys 625 and C-22.

Summary and Conclusions

Electrochemical polarization experiments were performed under potentiodynamic and potentiostatic control in an acidic brine at temperatures ranging between ambient and 90°C to evaluate the initiation and propagation of localized corrosion in candidate waste package inner container materials. The significant conclusions drawn from this investigation are given below:

- Nickel-rich Alloys 825 and G-3 exhibited pitting susceptibility in a 90°C acidic brine at $E_{cont} > E_{pit}$, the extent of pitting being more pronounced at higher E_{cont} values. Also, both materials suffered from crevice corrosion.

- Pits observed with Alloy G-3 were elongated, in contrast to round pits observed with Alloy 825. For Alloy 825, pits were located away from the crevice region, but some of the pits in Alloy G-3 were located within the crevice region.

- Tests performed at $E_{cont} > E_{corr}$ revealed crevice attack in Alloys 825, G-30, C-4 and 625 in a 30°C acidic brine without showing any pits. While Alloy C-22 was immune to localized attack in a similar test environment, slight crevice corrosion tendency was observed in this alloy at 60°C, suggesting its higher critical crevice corrosion temperature compared to other susceptible alloys tested.

- Alloy 625 showed crevice corrosion and surface attack in a 30°C acidic brine under combined potentiodynamic and potentiostatic control. But Alloy C-22 was not attacked under a similar test condition.

- Ti Grade-12 was immune to localized corrosion under all experimental conditions

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References

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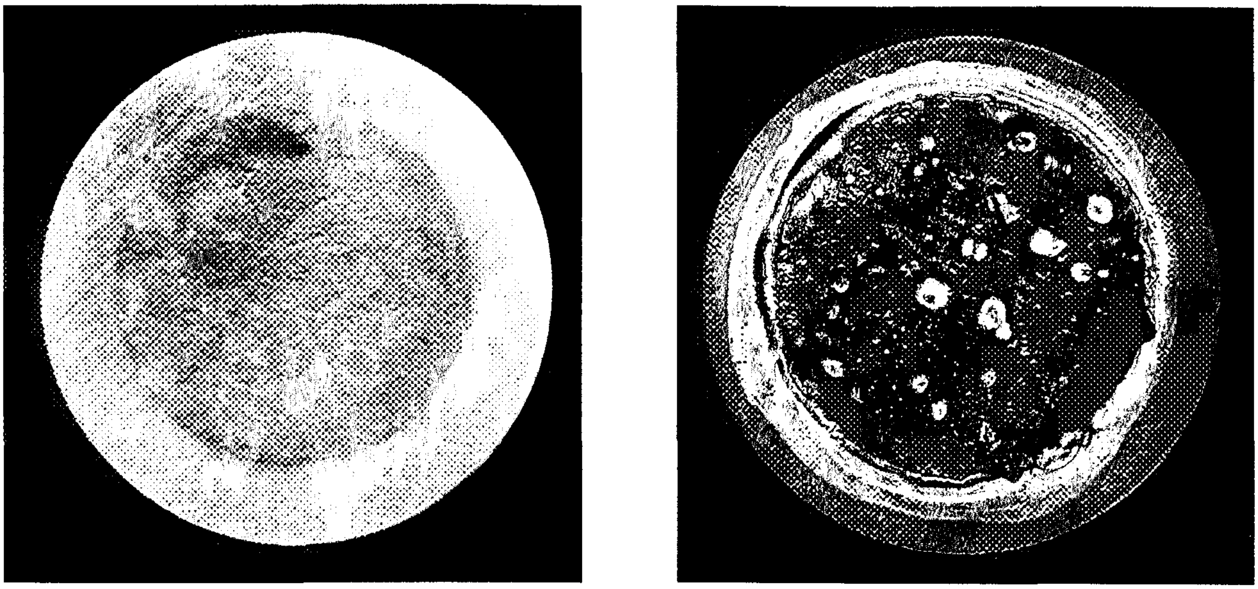
Table 1

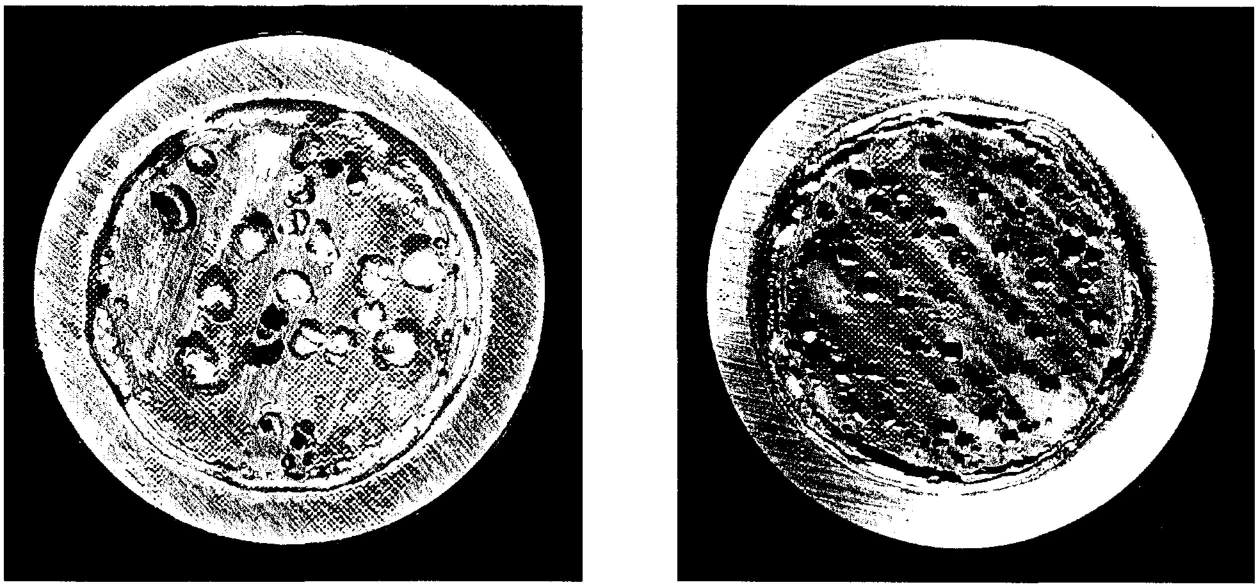
Chemical Composition of Materials Tested (wt%)

Material	Heat No.	C	Mn	P	S	Si	Ni	Cr	Mo	Fe	Ti	Al	Cu	Others
Alloy 825	HH3884FG	0.03	--	--	0.001	0.33	39.84	22.11	3.40	30.91	0.88	0.70	1.80	--
Alloy 825	L256	0.01	0.42	--	<.001	0.26	43.13	22.93	2.71	27.74	0.98	0.09	1.73	--
Alloy G-3	K914	0.004	0.80	0.009	0.003	0.36	46.33	22.26	6.88	19.29	--	--	1.90	Nb+Ta W: 0.8
Alloy G-30	L466	0.01	1.14	0.012	0.002	0.48	41.20	28.96	5.39	14.11	--	--	1.88	Nb+Ta W: 2.8
Alloy C-4	B033	0.003	0.21	<.005	<.002	0.04	Bal	15.68	15.38	0.77	0.24	--	--	--
Alloy C-22	J244	0.004	0.21	0.004	<.001	0.03	Bal	20.65	14.08	2.61	--	--	--	W: 3.2 Co: 0.1
Alloy 625	L704	0.02	0.08	0.006	0.001	0.08	Bal	21.67	8.90	3.86	0.27	0.29	--	Nb+Ta
Ti Grade-12	H427	0.012	--	--	--	--	0.80	--	0.30	0.14	Bal	--	--	--



E_{cont} : 150 mV (Ag/AgCl)
pH : 2.67 ; Test Duration : 480 min

E_{cont} : 160 mV (Ag/AgCl)
pH : 2.64 ; Test Duration : 232 min



E_{cont} : 170 mV (Ag/AgCl)
pH : 2.51 ; Test Duration : 218 min

E_{cont} : 180 mV (Ag/AgCl)
pH : 2.57 ; Test Duration : 240 min

Figure 1. Macroscopic View of Potentiostatically Polarized Alloy 825 Specimens in 90°C Acidic Brine at Various Controlled Electrochemical Potentials (E_{cont})

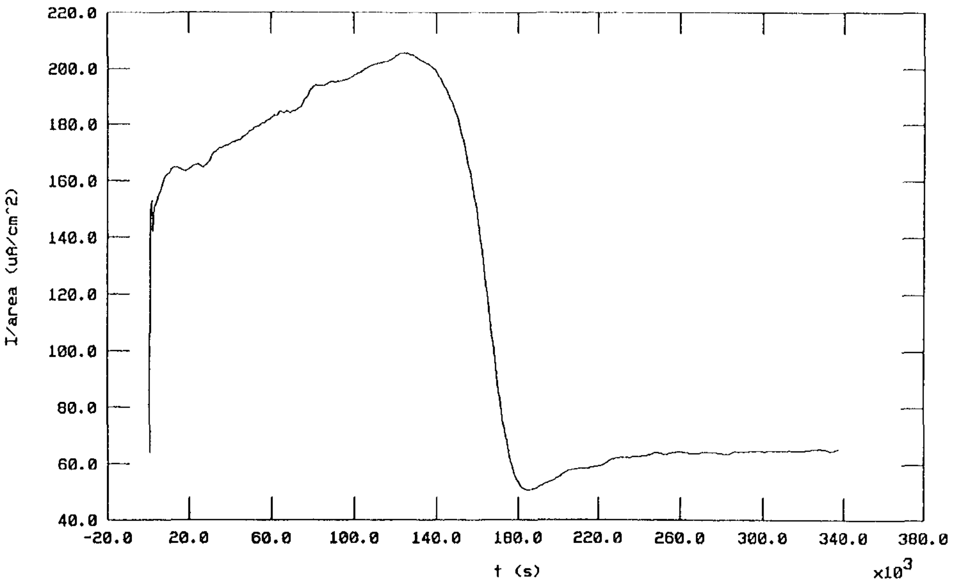


Figure 2. Potentiostatic Polarization Curve for Alloy C-22 in a 30°C Acidic Brine (pH≈2.69) at E_{cont} Value of 870 mV (Ag/AgCl)

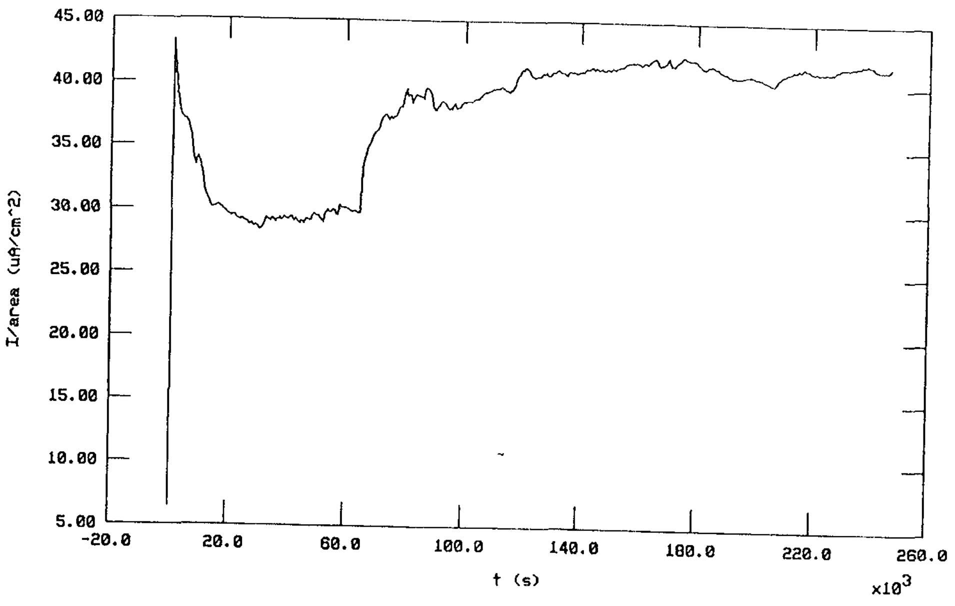


Figure 3. Potentiostatic Polarization Curve for Alloy 625 in a 30°C Acidic Brine (pH≈2.69) at E_{cont} Value of 854 mV (Ag/AgCl)

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University of California · Livermore, California 94551