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Evaluation of the Comparative Corrosion Resistance Between AKOT Ti Alloy and Ti Gr 7 Alloy

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Disclaimer

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INTRODUCTION

In its current design, the drip shields for the high-level nuclear waste containers for the Yucca Mountain repository will be mainly made using Ti Gr 7 (R52400). Ti Gr 7 is a highly corrosion resistant alloy, especially because it contains 0.15% palladium (Pd).

The goal of this study was to determine whether an AKOT low-Pd (0.01%) titanium alloy would have a similar corrosion resistance than the more expensive Ti Gr 7 in environments that could be related to the performance of the drip shield.

The focus of this testing program was on the susceptibility of the alloys to localized corrosion. Therefore, only artificially creviced specimens were used.

EXPERIMENTAL

Table 1 shows the chemical composition of the AKOT and Ti grade 7 specimens received from Kobe Steel.

Table 1. Chemical Composition (in wt.%) of AKOT and Ti Gr 7 Alloys.
The Balance of the composition is Titanium (>99%)

	Ni	Cr	Pd	Ru	Fe	C	O	N	H
AKOT	0.44	0.16	0.010	0.032	0.05	0.008	0.102	0.003	0.0092
Ti Gr 7	-	-	0.17	-	0.067	0.006	0.084	0.004	0.0003

The composition of Ti Gr 7 is given in ASTM standard B 265. According to B 265, the composition of AKOT Ti alloy would be similar to either Grades 33 or 34. The main difference between Ti Gr 7 and AKOT compositions is that the latter contains small amounts of Ru, Ni, Cr and also a lower content of Pd than Ti Gr 7.

The specimens used for corrosion testing were prism crevice assemblies (PCA). These specimens were 19×19×9.5 mm with a hole in the middle to attach the crevice formers (CF) (Figure 1). The fabricated specimens were supplied by Kobe Steel. Each specimen received at LLNL was wet ground with 600-grit SiC paper, and then ultrasonically cleaned in de-ionized water just before testing. The specimen was then sandwiched by a pair of serrated ceramic crevice formers (ASTM G 48), using a Ti bolt and nut to apply the desirable tightness or torque (70 in-lb). Part of Ti bolt was sleeved with Teflon tubing to prevent the Ti bolt from making electrical contact with the test specimen. The specimen was then mounted in a specimen holder with electrical connection to run the polarization studies (Figure 1). The final exposed surface area for the specimen after the crevice assembling was 14.06 cm^2.

A three-electrode cell (Figure 1), with a capacity of 1 liter, was used for all the experiments. Approximately 900 mL of electrolyte solution was used in each test. A saturated silver/silver chloride (Ag/AgCl, prefilled with 4 M KCl saturated with AgCl) reference electrode was used for measuring the potential of the working electrode. A solution bridge with a Luggin probe was used to maintain an ionic conductive path between the working electrode and the reference electrode, while a cooling jacket was used to maintain the reference electrode at near room temperature. A platinum (Pt) rod or sheet was used as a counter electrode. The electrochemical cell assembly was placed in a heating mantle to maintain the temperature of the test solution. An Allihn condenser was used to prevent solution evaporation. The electrochemical polarization measurements were conducted through a commercial potentiostat that was integrated with a desktop computer and the companion software.

The test solutions used in this study were 1 mol/L (or 1 M) NaCl brines. To study the effects of fluoride, 0.1 mol/L NaF was added into the NaCl brines. The solution pH was adjusted prior to each test to pH values of 4 or 8. The test temperature was 95°C. N_2 gas purging was used to de-aerate the test solutions. Gas purging began at least one-half hour before the specimens were placed into the solution. The test specimens were stabilized for 1 hour in the test solution before the electrochemical measurements were started.

Cyclic potentiodynamic polarization (CPP) measurements were performed to assess the localized corrosion susceptibility of both Ti Gr 7 and AKOT in NaCl brines with and without the presence of fluoride. A potential scan rate of 600 mV per hour was used for all polarization measurements (0.167 mV/s). The CPP technique is described in ASTM G 61.

Open-circuit potential (OCP) immersion tests were also performed to evaluate the resistance of the Ti alloys to corrosion as a function of time both in pure NaCl solutions and in fluorinated salt solutions. In these tests, the specimens were exposed to the test solution for up to two weeks. The free corrosion potential (E_{corr}) was monitored as a function of time, and polarization resistance (R_p) measurements were performed at various time increments during the exposure period. Post-test surface examinations determined the severity of corrosion in each tested specimen.

EXPERIMENTAL RESULTS

Table 2 shows a description of the tests conducted and the outcome of the testing results.

1. Corrosion resistance in acidic and neutral NaCl solutions

Based on the cyclic polarization measurement results (Figure 2), both AKOT and Ti Gr 7 alloys showed excellent resistance to localized corrosion in acidic (pH 4) 1M NaCl solutions at 95°C. AKOT and Ti Gr 7 had an identical electrochemical up to a potential of 1 volt. Above 1 volt their polarization behavior was different but these high potentials are of little interest for corrosion applications since they are above the stability of water. The high potential deviation between both materials only reflects the different surface chemistry for AKOT and Ti Gr 7 that supports the oxygen evolution reaction. No localized corrosion was observed on either AKOT or Ti Gr 7 specimens was observed after the tests (Table 2 and Figure 2) in spite that the specimens were polarized to very high potentials of near 5 volts. Only discoloration was observed on the surface.

Table 2 - Lists of tests and test results

Specimen ID	**Test Environment**	**Test Description**	**Observations after the tests**
A1 (AKOT)	1M NaCl + 0.1M NaF, pH 8, 95°C, de-aerated with N_2	2-weeks long immersion test (OCP monitoring)	General & crevice corrosion
A2 (AKOT)			General & crevice corrosion
B1 (Ti Gr 7)			General & crevice corrosion
A11 (AKOT)	1M NaCl + 0.1M NaF, pH 8, 95°C, aerated with CO_2-free air	10-days long immersion test (OCP monitoring)	General & crevice corrosion
A12 (AKOT)			General & crevice corrosion
B11 (Ti Gr 7)			General & crevice corrosion
B12 (Ti Gr 7)			General & crevice corrosion
A3 (AKOT)	1M NaCl + 0.1M NaF, pH 8, 95°C, de-aerated with N_2	Cyclic Potentiodynamic Polarization	Crevice corrosion
A4 (AKOT)			Crevice corrosion
B3 (Ti Gr 7)			Crevice corrosion
B4 (Ti Gr 7)			Crevice corrosion
A6 (AKOT)	1M NaCl, pH 4, 95°C, de-aerated with N_2	Cyclic Potentiodynamic Polarization	No localized corrosion
B5 (Ti Gr 7)			No localized corrosion
B6 (Ti Gr 7)			No localized corrosion
A8 (AKOT)	1M NaCl, pH 8, 95°C, de-aerated with N_2	Cyclic Potentiodynamic Polarization	No localized corrosion
B7 (AKOT)			No localized corrosion
B8 (Ti Gr 7)			No localized corrosion
A9 (AKOT)	1M NaCl + 0.1M NaF, pH 8, 95°C, de-aerated with N_2	Potentiostatic test with applied potential of –0.25 V (Ag/AgCl)	Crevice corrosion
A10 (AKOT)			Crevice corrosion
B9 (Ti Gr 7)			Crevice corrosion
B10 (Ti Gr 7)			Crevice corrosion

The cyclic polarization measurements in neutral (pH 8) 1M NaCl solutions showed very similar results as in pH 4 solutions (Figure 3). The anodic behavior of both type of materials (Ti Gr 7 and AKOT) were practically identical up to a polarization of 1 volt. Again, both type of specimens showed slight discoloration after the tests but total absence of localized corrosion in spite of the high applied potential (Figure 3 and Table 2).

2. Corrosion behavior in fluoride-containing environments

Both AKOT and Ti Gr 7 materials were susceptible to general and localized corrosion in neutral (pH 8) 1 M NaCl solutions with addition of 0.1 M NaF at 95°C (Table 2). This was observed both after the cyclic polarization tests and after exposure to the free corroding potential (OCP tests) (Table 2).

Figure 4 shows the cyclic polarization curves of both materials in 1 M NaCl + 0.1 M NaF pH 8 solution at 95°C. Due to the effect of the added fluoride, the maximum polarization in Figure 4 was only approximately 0.2 V compared to Figures 2 and 3 (in pure NaCl solutions) in which the polarization was in the order of 5 volts. However, Figure 4 shows that the polarization behavior of both materials (Ti Gr 7 and AKOT) was the same in the fluorinated solution. Figure 4 also shows that in spite of the slight polarization, both materials suffered crevice corrosion under the tested conditions. Besides localized corrosion, both materials also underwent significant general corrosion (Table 2 and Figure 4).

The susceptibility of crevice corrosion attack in fluoride-containing solutions was also confirmed in the potentiostatic polarization measurements. In these tests a constant potential of –0.25 V (Ag/AgCl) was applied for sixty hours while the output current was recorded. Figure 5 shows that both materials behaved the same, that is, their dissolution rate was the same as a function of time. After 10-h exposure the dissolution rate of Ti Gr 7 was slightly higher than the dissolution rate of AKOT. Both AKOT and Ti Gr 7 materials showed corrosion attacks along the edge of crevice teeth, and on the bulk surface away from the crevice regions as well (Table 2 and Figure 5).

The localized corrosion of AKOT and Ti Gr 7 materials in fluoride-containing environments can also be initiated without the help of external polarization (Table 2). Figure 6 shows the corroded coupons after a 2-week immersion in deaerated 1 M NaCl + 0.1 M NaF solution of pH 8 at 95°C. The observations in the open-circuit immersion tests revealed that corrosion attack without the external polarization was mostly along the crevice formers edges, and that the general corrosion on the bulk surfaces was relatively minimal (Figure 6). It is apparent that the attack along the edges of the crevice formers was shallower for the AKOT specimen.

Figure 7 shows the evolution of the inverse of the resistance to polarization (Rp) as a function of time for specimens immersed in deaerated 1 M NaCl + 0.1 M NaF solution of pH 8 at 95°C. The inverse of Rp is proportional to the corrosion rate. Figure 7 shows that the corrosion rate of both alloys decreases as the time increases, probably because the materials are developing a more protective passive film on the surface. That is, in spite that these alloys suffered slight localized corrosion (Figure 6), their overall dissolution rate was decreasing as a function of time.

Similar tests were also conducted in aerated solutions (Table 2). The results from the aerated solutions were very similar to the ones from the de-aerated solutions (Figures 6 and 7). The dissolved oxygen level in the solutions did not influence the corrosion attack caused by the fluoride ions. The corrosion rate decreased slightly while the corrosion potential increased as immersion duration increased.

SUMMARY AND CONCLUDING REMARKS

This corrosion study on AKOT and Ti Gr 7 materials can be summarized as follows

- AKOT and Ti grade 7 showed similar corrosion resistance in NaCl solutions with and without fluoride
- Both AKOT and Ti Gr 7 are resistant to crevice corrosion in 1M NaCl solutions
- Both AKOT and Ti Gr 7 are susceptible to crevice corrosion in fluoride-containing aqueous solutions.

The comparison of the relative corrosion resistance of AKOT and Ti Gr 7 was made in a relative narrow electrolyte chemistry range. The finding here may not be applicable in other environments with very different water chemistries. It is likely that the pure NaCl solution was too benign for both alloys and the solution containing 0.1 M NaCl was too aggressive. Therefore, the corrosion behavior of these two alloys was not discriminated.

Other important corrosion property for AKOT and Ti Gr 7 not studied is their resistance to hydrogen-related degradation. For Ti Gr 7 or AKOT to be candidate for drip shield applications, the resistance to hydrogen absorption, hydride formation, and hydrogen embrittlement may be more important than the resistance of general and crevice corrosion.

ACKNOWLEDGMENTS

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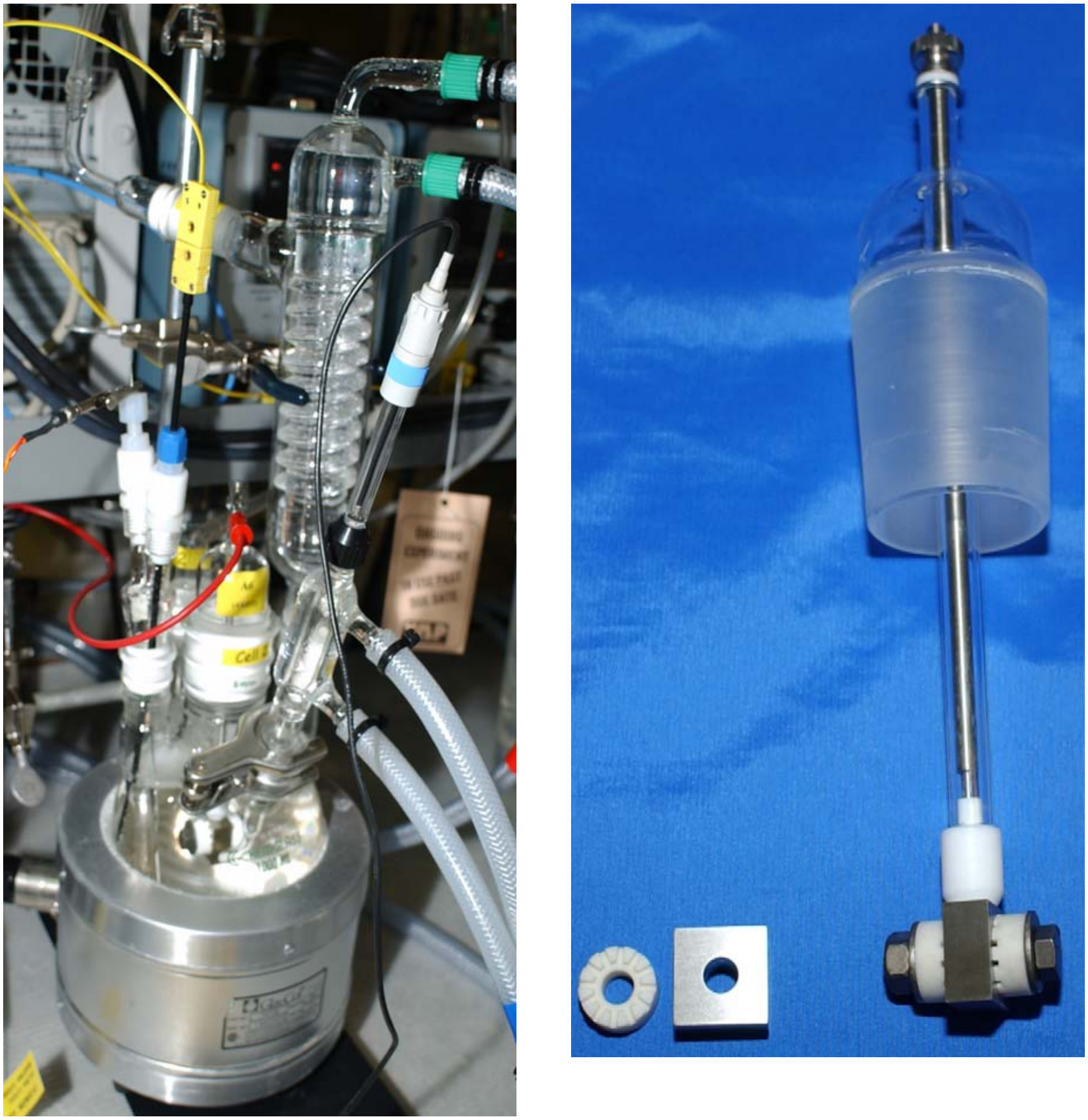
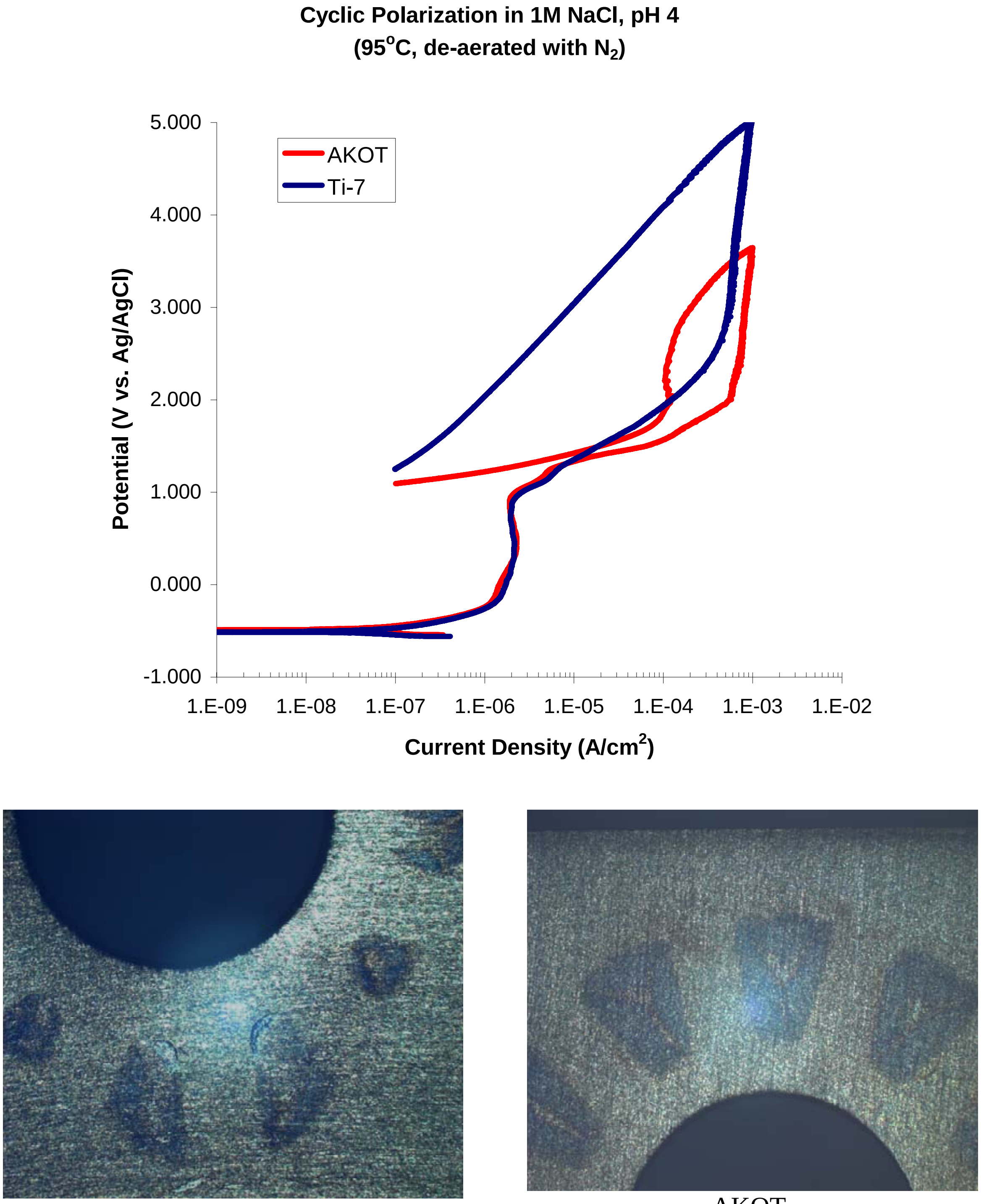


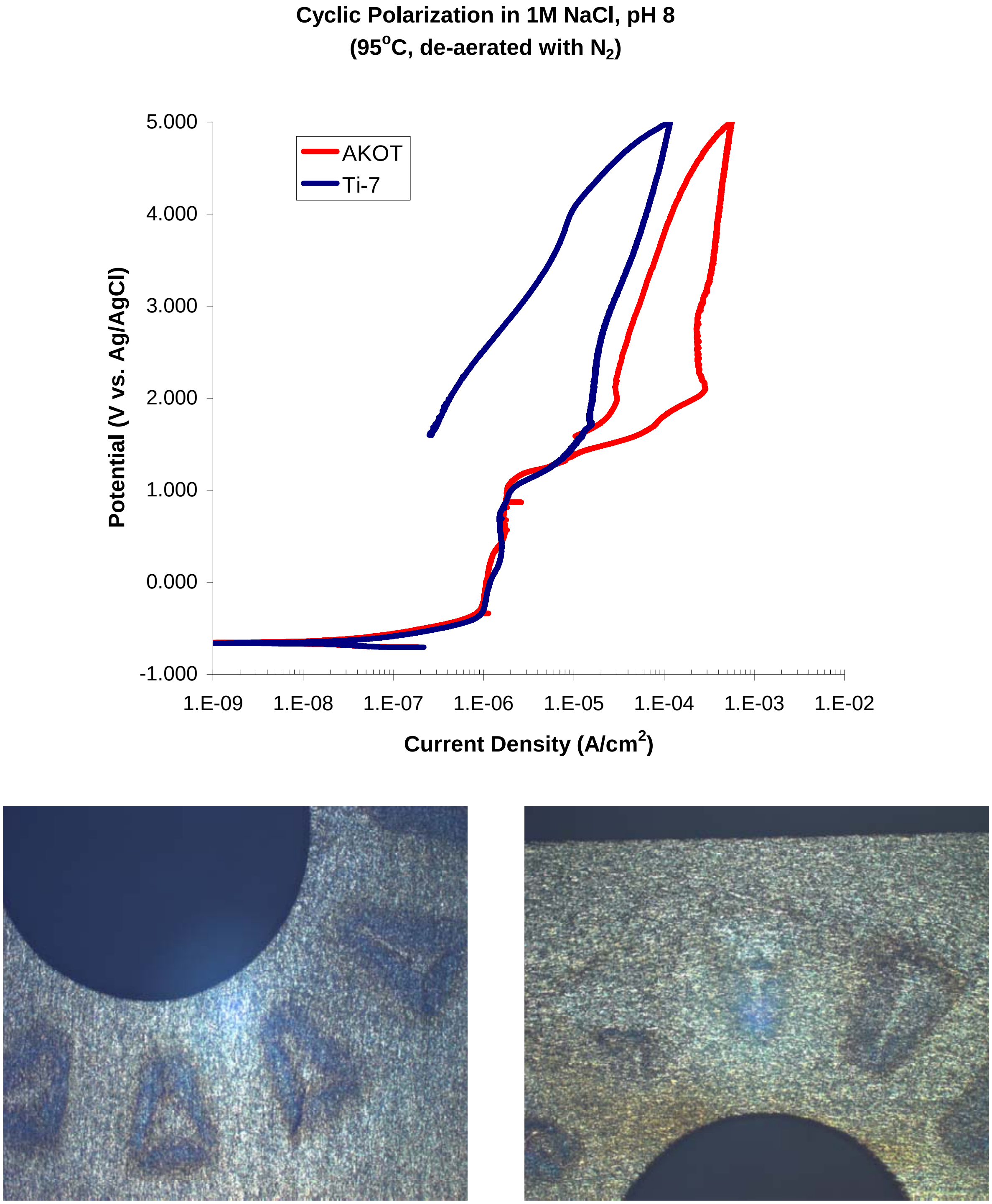
Figure 1 – Specimen and Experimental Apparatus for Electrochemical Testing



Ti Gr 7

AKOT

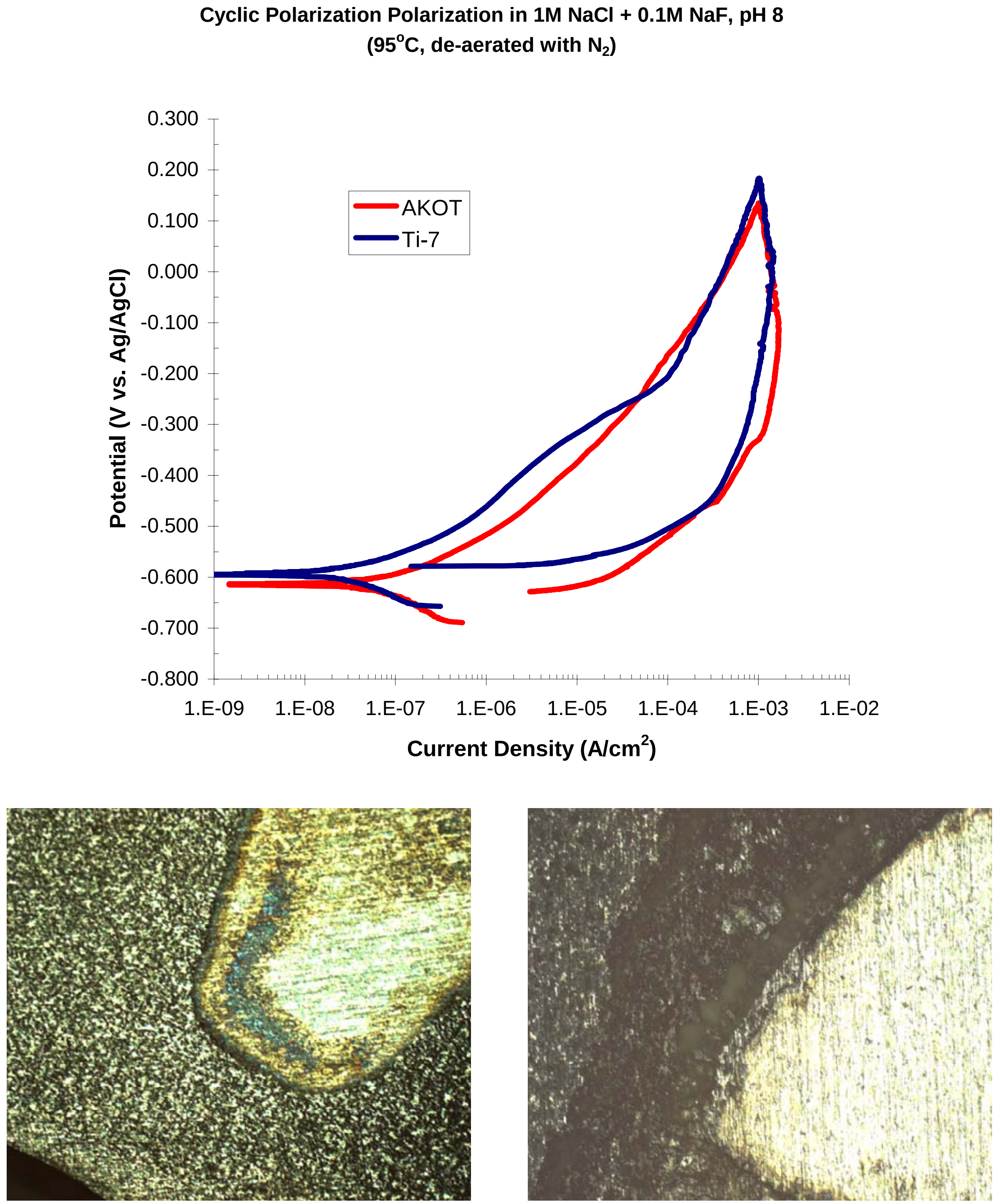
Figure 2 – Cyclic Potentiodynamic Polarization of Ti Gr 7 and AKOT in 1 M NaCl, pH 4 at 95°C.
The specimens were free from localized corrosion after the tests.


Cyclic Polarization in 1M NaCl, pH 8
(95^{o}C, de-aerated with N_2)

Ti Gr 7

AKOT

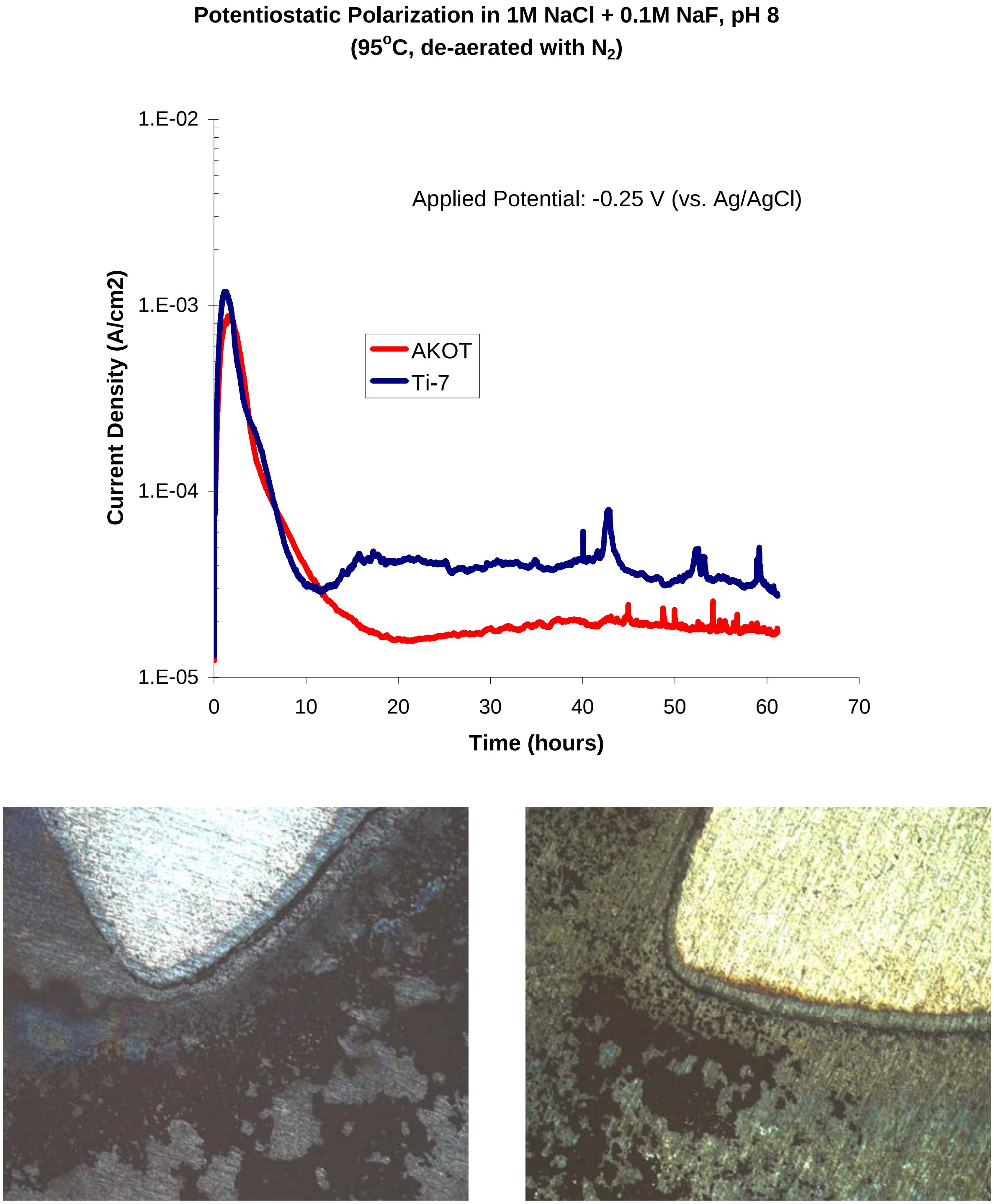
Figure 3 – Cyclic Potentiodynamic Polarization of Ti Gr 7 and AKOT
in 1 M NaCl, pH 8 at 95°C.
The specimens were free from localized corrosion after the tests.



Ti Gr 7

AKOT

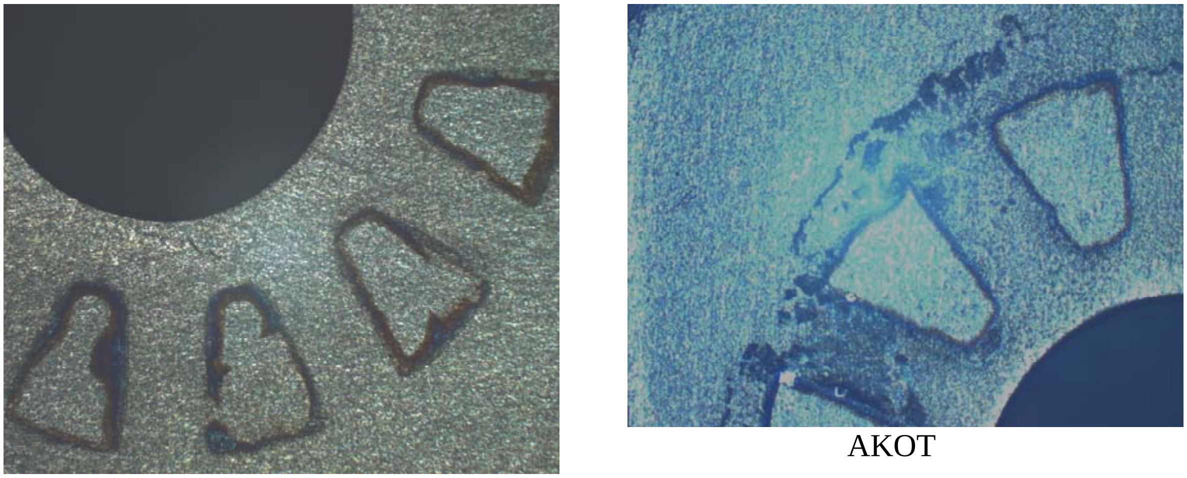
Figure 4 – Cyclic Potentiodynamic Polarization of Ti Gr 7 and AKOT in 1 M NaCl + 0.1 M NaF, pH 8 at 95°C.
The specimens showed localized corrosion after the tests.



Ti Gr 7

AKOT

Figure 5 – Potentiostatic Tests (-0.25 V) of Ti Gr 7 and AKOT
in 1 M NaCl + 0.1 M NaF, pH 8 at 95°C.
The specimens showed localized corrosion after the tests.



Ti Gr 7

AKOT

Figure 6 – Open Circuit Potential (OCP) tests of Ti Gr 7 and AKOT
in deaerated 1 M NaCl + 0.1 M NaF, pH 8 at 95°C. Test lasted 2 weeks.
The specimens showed contained localized corrosion after the tests.

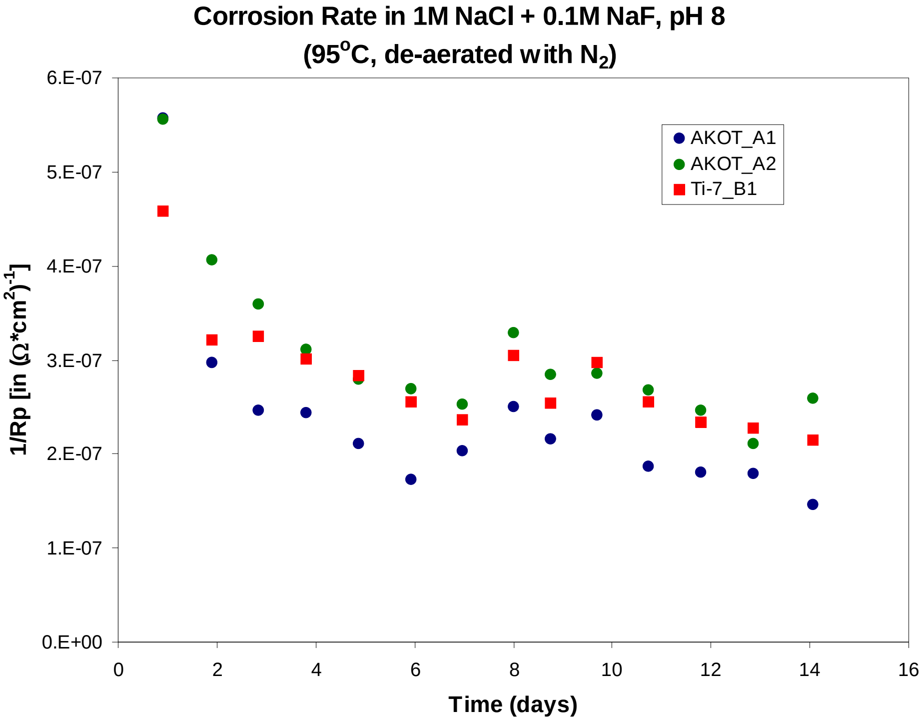


Figure 7 – Evolution of the corrosion current as a function of time for Ti Gr 7 and AKOT
exposed to deaerated 1 M NaCl + 0.1 M NaF, pH 8 at 95°C.
The corrosion rate slightly decreased as the exposure time increased.
The specimens showed contained localized corrosion after the tests (Figure 6).