ELECTROCHEMICAL BEHAVIOR AND PASSIVITY OF TITANIUM GRADES 7 AND 29 UNDER IMMERSION CONDITIONS

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ABSTRACT

This report documents the results of experimental studies that were conducted to evaluate the difference in corrosion behavior between Titanium Grades 7 and 29 under immersion conditions. In the proposed Yucca Mountain repository, titanium alloys (Grades 7 and 29) would be used to fabricate the drip shield, which is one of the engineered barriers. Because of the lack of long-term corrosion rates data for Titanium Grade 29, the U.S. Department of Energy (DOE) assumed that the corrosion rates for the Titanium Grade 29 structural supports are the same as those for the outer surface of the Titanium Grade 7 plate. This work was conducted to understand the difference in electrochemical behavior and passive film properties between Titanium Grades 7 and 29.

Cathodic and anodic polarization techniques were used to examine the electrochemical behavior of Titanium Grades 7 and 29 at 95 °C [203 °F] in a simulated crevice solution containing deaerated 5 M NaCl and 0.1 M HCl. The open circuit potential for Titanium Grade 29 was about 50 mV lower than that for Titanium Grade 7, but it was about 390 mV higher than that of commercially pure titanium, suggesting that the ruthenium addition to titanium passivated the material significantly, but the passivity was slightly lower than that with palladium addition. Both palladium in Titanium Grade 7 and ruthenium in Titanium Grade 29 influenced the proton reduction kinetics resulting in enhancement of the crevice corrosion resistance; however, palladium and ruthenium appeared not to influence much of the anodic dissolution behavior. The electrochemical impedance spectroscopy tests were conducted to study the passive film resistance in Yucca Mountain repository-relevant chemistries. The results indicated high passivity for both materials, and the passive film resistance appeared to be independent of temperature. Compared to Titanium Grade 7, Titanium Grade 29 showed lower passive film resistance; however, the difference is not significant.

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: All CNWRA-generated original data contained in this report meet the quality assurance requirements described in the Geosciences and Engineering Division Quality Assurance Manual. Sources for other data should be consulted for determining the level of quality for those data. All data and calculations related to this report have been recorded in CNWRA Scientific Notebooks 794 (He, 2011a) and 1024E (He, 2011b).

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1 INTRODUCTION

This report is part of the knowledge management activities for the U.S. Nuclear Regulatory Commission (NRC) high-level waste repository safety program. The report documents experimental work to assess the difference in electrochemical behavior and passive film properties between Titanium Grades 7 and 29.

1.1 Background

In the proposed Yucca Mountain repository (DOE, 2008), the titanium alloy (Grades 7 and 29) drip shields and Alloy 22 (Ni−22Cr−13Mo−3W−4Fe) waste package outer containers are components of the engineered barrier system. The drip shield is designed to divert water that could have entered the drift and prevent the water from contacting the waste package. DOE (2008) stated that the drip shield plates will be fabricated from Titanium Grade 7 (UNS R52400). Titanium Grade 7 is a commercially pure titanium alloy with the addition of a small amount of palladium (approximately 0.2 wt%) to enhance its corrosion resistance. The drip shield structural supports will be fabricated from Titanium Grade 29 (UNS R56404), which is a titanium alloy composed of approximately 6 wt% aluminum and 4 wt% vanadium for strength, plus approximately 0.1 wt% ruthenium for corrosion resistance.

Titanium is highly resistant to corrosion in a wide range of environments conferred by the naturally formed passive film on the surface. However, as pH decreases and temperature increases, titanium passivity decreases resulting in decreasing corrosion resistance, especially crevice corrosion resistance. One of the most effective strategies for enhancing the corrosion resistance, especially in a reducing acidic environment such as the crevice region, is through alloying with platinum group metals (platinum, palladium, rhodium, ruthenium, iridium, and osmium) (Schutz, 2003). Among the platinum group metals, platinum and ruthenium are commonly used as the alloying elements. It is generally accepted that the function of these noble metal elements is to create cathodic sites, which catalyze proton reduction in the reducing acidic environment. As schematically shown in Figure 1-1, this catalysis of proton reduction shifts the corrosion potential into the passive region, thereby enhancing the corrosion resistance.

Although both palladium and ruthenium can enhance titanium corrosion resistance, Schutz (2003) indicates that for the same amount of alloying elements, palladium is more effective in enhancing corrosion resistance than ruthenium. Ruthenium content needs to be approximately twice that of palladium to achieve equivalent corrosion resistance. The difference could be because of the different catalysis capabilities of palladium and ruthenium. For titanium materials, because the ruthenium content in Titanium Grade 29 is less than the palladium content in Titanium Grade 7, the corrosion resistance of Titanium Grade 29 could be lower than that of Titanium Grade 7 based on the observation by Schutz (2003).

Figure 1-1. Schematic Illustrating the Polarization Curve for Titanium and its Relationship to the Cathodic Polarization Curves for Proton Reduction on Unalloyed Titanium and on a Platinum Group Metal Alloyed Titanium

1.2 Objective

Because of the presence of different alloying elements in Titanium Grades 7 and 29, and scarcity of data available in the literature to evaluate the corrosion behavior of Titanium Grade 29, the objective of this work is to investigate the possible different electrochemical behavior and passivity of Titanium Grades 7 and 29 under immersion conditions. The results are used to evaluate the difference in passive film properties between Titanium Grades 7 and 29.

2 EXPERIMENTS

Electrochemical polarization and impedance spectroscopy were used to understand the possible difference in corrosion resistance properties of Titanium Grades 7 and 29. Experiments were carried out with cylindrical specimens 6.2 mm [0.24 in] in diameter and 48 mm [1.9 in] in length machined from the same Titanium Grades 7 and 29 as for the dripping tests.¹ The Titanium Grade 7 is in mill-annealed condition with a single α-phase conforming to ASTM B265 (ASTM International, 2008). The Titanium Grade 29 is in the β-transformed (final processed above the β-transus temperature) plus subsequently annealed condition conforming to ASTM B861 (ASTM International, 2010). The Titanium Grade 29 has an α-plus-β phase structure. Both titanium grades were used as in the as-received condition without any heat treatment. In the prototype drip shield design, DOE proposed to heat treat the drip shield assembly to relieve stress from the fabrication process at 593 °C [1,100 °F] for a minimum of 2 hours (BSC, 2007). Heat treatment below the β-transus temperature is not expected to affect the corrosion properties. The chemical composition of the titanium specimens used in this study is shown in Table 2-1. All specimens were polished up to a 600-grit finish and cleaned ultrasonically in deionized water and acetone. At the completion of each test, the specimens were rinsed in deionized water and dried.

2.1 Cathodic and Anodic Polarization

To understand the role of palladium in Titanium Grade 7 and ruthenium in Titanium Grade 29 on corrosion resistance properties of the alloys, the cathodic and anodic polarization behaviors of Titanium Grades 7 and 29 were examined at 95 °C [203 °F] in a simulated crevice solution containing 5 M NaCl and 0.1 M HCl deaerated with ultra high purity N_2 . The test solution and temperature were the same as those Brossia and Cragnolino (2004) and Brossia, et al. (2001) used to examine the electrochemical behavior difference between Titanium Grades 2 and 7 (Titanium Grade 2 is commercially pure titanium without any noble alloy element addition). During the tests, about 38 mm [1.5 in] out of the 48 mm [1.9 in] cylindrical specimen was immersed in solution. The cathodic polarization tests were performed from 100 mV above the open circuit potential down to −0.8 V_{SCF} at the same scan rate as the anodic polarization tests. In a separate test, anodic polarization tests were performed from 100 mV below the open circuit potential up to 1.0 V_{SCE} at a scan rate of 0.167 mV/s. All the polarization tests were conducted in a glass cell with a 200-mL [0.053-gal] solution. The cells were fitted with a water-cooled condenser and a water trap to minimize solution loss at elevated temperatures and by air intrusion. The saturated calomel reference electrode was connected to the solution through a water-cooled Luggin probe with a porous silica tip, and the reference electrode was maintained at room temperature. A platinum flag was used as a counter electrode.

2.2 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy tests were conducted in 2-L [0.53-gal] glass cells with polytetrafluoroethylene lids. The cell has the same configuration as that for the polarization tests. The groundwater chemistries relevant to the Yucca Mountain repository including simulated concentrated water and simulated acidified water were used in the test (Gordon, 2002). Table 2-2 summarizes the chemical composition of simulated concentrated

 ¹Jung, H., X. He, T. Ahn, T. Mintz, and R. Pabalan. "Corrosion of Alloy 22 and Titanium Alloys Under Seepage Water Dripping Conditions." San Antonio, Texas: CNWRA. 2011. Under NRC review.

*Ti—titanium, Pd—palladium, Fe—iron, C—carbon, N—nitrogen, O—oxygen, H—hydrogen, Al—aluminum, V—vanadium, Ru—ruthenium, N/A—not applicable

 $*$ 1 g/L = 8.35 × 10^{−3} lb/gal

water and simulated acidified water. Simulated concentrated water has a pH ranging from 9.8 to 10.2. The pH of simulated acidified water is around 2.7. For one set of tests in simulated concentrated water, the solution was deaerated with ultra high purity N_2 . All other tests were open to air through the condenser. During the test, 41 mm [1.5 in] out of the 48 mm [1.9 in] cylindrical specimen was immersed in solution. Electrochemical impedance spectra were obtained at open circuit over a frequency range of 100,000 to 0.001 Hz at temperatures of 60, 80, and 95 °C [140, 176, and 203 °F] sequentially. At each temperature the impedance spectra were measured about once each week up to several times. After the impedance measurements at each temperature, the solution was set to the next higher temperature. The total duration for each test was about 2 months.

3 RESULTS AND DISCUSSION

3.1 Cathodic and Anodic Polarization

Figure 3-1 shows the cathodic polarization curves for Titanium Grades 7 and 29 obtained from deaerated 5 M NaCl and 0.1 M HCl solution at 95 °C [203 °F]. Table 3-1 summarizes the open circuit potentials and cathodic Tafel slopes of Titanium Grades 7 and 29 obtained from this study and those of Titanium Grade 2 that Brossia, et al. (2001, Figure 4-19) previously obtained under the same conditions. The open circuit potential for Titanium Grade 29 was about 50 mV lower than that for Titanium Grade 7, but it was about 390 mV higher than that of Titanium Grade 2. This suggests that the ruthenium addition to titanium passivated the material significantly. For both Titanium Grades 7 and 29, an activation-controlled region was observed that was then followed by a mass-transport-limited region. In the activation-controlled region, Titanium Grade 7 exhibited a cathodic Tafel slope of −32 mV/decade (Figure 3-1), which is similar to −27 mV/decade Brossia, et al. (2001) measured. In this region, Titanium Grade 29 appeared to show two subregions with a cathodic Tafel slope of −57 mV/decade at lower overpotentials followed by −22 mV/decade at higher overpotentials. The average value is close to that of Titanium Grade 7 suggesting palladium and ruthenium have a smiliar effect on cathodic behavior of titanium. The minor difference could be due to the difference in microstructure with Titanium Grade 7 exhibiting single phase and Titanium Grade 29 exhibiting two phases. The absolute value of cathodic Tafel slopes for Titanium Grades 7 and 29 was smaller than that of Titanium Grade 2 (−100 mV/decade), which suggests that the palladium or ruthenium facilitated the cathodic reaction (proton reduction) in this study (i.e., a small change in

Figure 3-1. Cathodic Polarization Curves of Titanium Grades 7 and 29 in a Simulated Crevice Solution of Deaerated 5 M NaCl, and 0.1 M HCl at 95 °C [203 °F]

potential applied to Titanium Grades 7 or Grade 29 leads to a large change in current). Schutz (2003) indicated that this facilitated cathodic depolarization shifts the alloy potential in the noble direction where oxide film passivation is possible. This study shows that both palladium and ruthenium influenced the cathodic reaction kinetics and both Titanium Grades 7 and 29 will have higher crevice corrosion resistance than Titanium Grade 2.

Figure 3-2 shows the anodic polarization curves of Titanium Grades 7 and 29 obtained from deaerated 5 M NaCl and 0.1 M HCl solution at 95 °C [203 °F]. The open circuit potential is summarized in Table 3-1 along with that of Titanium Grade 2 Brossia, et al. (2001, Figure 4-20) previously obtained under the same conditions. Consistent with the cathodic polarization behavior, Titanium Grade 7 exhibited slightly higher open circuit potential. Both materials exhibited essentially passive behavior at all potentials above the corrosion potential. Titanium Grade 29 showed slightly higher anodic current at lower potential, but it decayed to values close

Figure 3-2. Anodic Polarization Curves of Titanium Grades 7 and 29 (Brossia, et al., 2001, Figure 4-20) in a Simulated Crevice Solution of Deaerated 5 M NaCl and 0.1 M HCl at 95 °C [203 °F]

to that of Titanium Grade 7. The anodic behavior of both Titanium Grades 7 and 29 was similar to that of Titanium Grade 2 (Brossia, et al., 2001) suggesting that palladium and ruthenium in Titanium Grades 7 and 29 are unlikely to influence anodic dissolution behavior of the alloys.

3.2 Electrochemical Impedance Spectroscopy

Figure 3-3 shows the Bode and Nyquist plots of the frequency response of the Titanium Grades 7 and 29 as a function of temperature in $N₂$ -deaerated simulated concentrated water. The Nyquist plots are typical for passive materials with high passive film resistance, which did not show a semicircle. At each temperature the impedance measured was reproducible, and the impedance response was not affected by temperature. The phase angle spectra in the Bode plots seem to suggest that the oxide had two layers, one possibly transformed from the original passive layer upon contact with solution. However, the two layers were not very distinctive. For simplification, the spectra were fit to an analog equivalent circuit with one-time constant shown in Figure 3-4. The polarization resistance corresponding to the passive film resistance from fitting the spectra is summarized in Table 3-2. The average film resistance from all three temperatures for Titanium Grade 7 was almost two orders of magnitude higher than that of Titanium Grade 29, indicating lower passivity for Titanium Grade 29 under the same test conditions. After the test the specimen appeared darker, but no localized corrosion was observed.

Tests were also conducted in simulated concentrated water and simulated acidified water under aerated condition. Similar to what was observed from Figure 3-3, the impedance response was not affected by temperature. (The spectra from aerated simulated concentrated water are not shown, because they were similar to Figure 3-3.). The Titanium Grade 7 specimen showed higher film resistance suggesting higher passivity for Titanium Grade 7 under the test conditions. The spectra were also fit to the analog equivalent circuit shown in Figure 3-4, and Table 3-3 summarizes the passive film resistance from fitting the spectra. The average film resistance for Titanium Grade 7 is less than one order of magnitude higher than that of Titanium Grade 29.

The Bode plots of the frequency response of the Titanium Grades 7 and 29 specimens in aerated simulated acidified water at 60 °C [140 °F] are shown in Figure 3-5 (data from other temperatures were not included because they were too noisy). In the impedance magnitude spectra, the spectroscopy for Titanium Grade 7 was slightly greater than that for Titanium Grade 29 indicating that Titanium Grade 29 has slightly lower passive film resistance. The posttest specimens are shown in Figure 3-6. For the test from simulated concentrated water, the surface was covered by a layer of white deposits from the solution. For the test from simulated acidified water, deposits were only shown at the interface of solution and vapor. No pitting corrosion was observed from either test.

Both the polarization and electrochemical impedance spectroscopy show that Titanium Grade 29 had lower passive film resistance than Titanium Grade 7. The dripping tests¹ at 95 °C [203 °F] and 75 percent relative humidity showed that Titanium Grade 29 had higher corrosion rate, which could be attributed to the lower passive film resistance. The observation from this study is different from that Andresen and Kim (2006) reported whereby the corrosion resistance for Titanium Grades 7 and 29 was nearly identical.

 ¹Jung, H., X. He, T. Ahn, T. Mintz, and R. Pabalan. "Corrosion of Alloy 22 and Titanium Alloys Under Seepage Water Dripping Conditions." Under NRC review. San Antonio, Texas: CNWRA. 2011. Under NRC review.

(a)

Figure 3-3. (a) Bode Plots and (b) Nyquist Plots of Electrochemical Impedance Spectra Recorded on Titanium Grades 7 and 29 in N2-Deaerated Simulated Concentrated Water at 60, 80, and 95 °C [140, 176, and 203 °F]

(b)

Figure 3-3 (continued). (a) Bode Plots and (b) Nyquist Plots of Electrochemical Impedance Spectra Recorded on Titanium Grades 7 and 29 in N₂-Deaerated Simulated Concentrated Water at 60, 80, and 95 °C [140, 176, and 203 °F]

Figure 3-4. One-Time Constant Analog Circuit Model for Fitting Electrochemical Impedance Spectroscopy Data

Note: R_s—Solution resistance; R_p—Polarization resistance; CPE—Constant **Phase Element**

Figure 3-5. Bode Plots of Electrochemical Impedance Spectra Recorded on Titanium Grades 7 and 29 in Aerated Simulated Acidified Water at 60 °C [140 °F]

Figure 3-6. Posttest Titanium Grades 7 and 29 Specimens From (a) Simulated Concentrated Water and (b) Simulated Acidified Water

4 SUMMARY AND CONCLUSIONS

In the proposed Yucca Mountain repository (DOE, 2008), the titanium alloy (Grades 7 and 29) drip shield is an engineered barrier designed to divert water that enters the drift and prevent it from contacting the waste package. The corrosion resistance of Titanium Grades 7 and 29 is enhanced by adding a small amount of palladium and ruthenium, respectively. This work was conducted to understand the difference in electrochemical behavior and passive film properties between Titanium Grades 7 and 29.

To understand how palladium affects the electrochemical behavior of Titanium Grade 7 and ruthenium affects Titanium Grade 29, the cathodic and anodic polarization behaviors of Titanium Grades 7 and 29 were examined at 95 °C [203 °F] in a simulated crevice solution containing deaerated 5 M NaCl and 0.1 M HCl. The open circuit potential for Titanium Grade 29 was about 20 mV lower than that for Titanium Grade 7, but it was about 390 mV higher than that of Titanium Grade 2, suggesting that the ruthenium addition to titanium passivated the material significantly, but the passivity was lower than that with palladium addition. Both palladium and ruthenium influenced the cathodic reaction kinetics and both Titanium Grades 7 and 29 will have higher crevice corrosion resistance than Titanium Grade 2. Palladium and ruthenium did not appear to influence much of the anodic dissolution behavior compared to Titanium Grade 2.

The electrochemical impedance spectroscopy tests were conducted to study the passive film resistance. The groundwater chemistries relevant to Yucca Mountain including simulated concentrated water and simulated acidified water were used in the test. The impedance response from both materials was typical for passive materials with high oxide film resistance. The passive film resistance was not affected by temperature. The Titanium Grade 7 specimen showed higher film resistance indicating higher passivity for Titanium Grade 7 under the test conditions.

In summary, both polarization and electrochemical impedance spectroscopy show that Titanium Grade 29 had lower passive film resistance than Titanium Grade 7. However, both tests show that Titanium Grades 7 and 29 had high passivity. Compared to the difference between Titanium Grade 7 and commercially pure titanium, the difference between Titanium Grades 7 and 29 is not significant.

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