Enhanced Shielding Performance of HLW Storage Packages via Multi-Component Coatings

Fuel Cycle Research and Development
Leigh Winfrey*
Virginia Polytechnic Institute and State University

B.P. Singh, Federal POC
Ken Sorenson, Technical POC

*University of Florida at the time of publication
1. COVER PAGE DATA ELEMENTS

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<td>Principle Investigator</td>
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<tr>
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<td>1800 Pratt Drive Suite 2006 (0170)</td>
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<tr>
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2. PROPRIETARY DATA STATEMENT

Given a number of pending journal articles and proceedings, the data regarding coating components and their behavior should be considered proprietary until published.
3. EXECUTIVE SUMMARY

The steel coatings developed here prevent water, dirt, and chemical contaminants from the atmosphere or soil from making contact with waste packages that would damage and weaken them during long-term storage. In addition, through this project we demonstrated that a range of coatings have this capability, will survive in the environment they will be used in, and can be deposited readily on large surfaces which is critical for their use in waste storage.

4. COMPARISON OF OBJECTIVES

The objective of this research was to develop an outer shield material for use in packaging that is not only resistant to the corrosion, radiation, diffusion, and thermal cycling processes that affect fuel packages during long term storage, but that is also wear tolerant and mechanically robust so that it can survive repeated handling and transportation.

Through the course of this research effort, we examined a range of candidate materials and developed a set of materials that protect steel in warm, moist, and radiation environments. Rather than one specific material, we have developed a range of materials that can be suitable for different applications, all of which improve steel performance. Generally, the best materials contain a small amount of zirconia and roughly equal portions of titania and alumina.
5. SUMMARY OF PROJECT ACTIVITIES

Deposition and Surface Morphology

The multi-layer barrier concept, as shown in Fig. 1, is a technique to coat the HLW canister with three layers starting with a diffusion barrier from TiN coating, followed by a corrosion barrier from zirconolite (ZrO$_2$-TiO$_2$-Al$_2$O$_3$) and an outer MoS$_2$ friction-tolerant / anti-cracking coating. As shown in Fig. 1 the multilayer section is about 50µm thick, however, the thickness can be increased provided good adhesion between then layers and the waste package. Planar cathodic sputter deposition system has been used to deposit TiN and laser ablation-deposition was used to deposit ZrO$_2$ on SS 316, 304 and A36 carbon steel. Fig. 2 illustrates the sputter-deposition technique when using planar cathodic sputter deposition system. A photograph of the Magnetron sputtering system is shown in Fig. 3.

![Multilayer protective coatings for high-level waste storage (not to scale)](image1)

![Planar cathodic sputter deposition configuration](image2)
Fig. 3 Magnetron sputtering system used for deposition of TiN, ZrO$_2$ and MoS$_2$.

TiN coating on SS316 substrate

ZrO$_2$ coated on top of TiN on SS316

Fig. 4 SEM and EDXA of coated samples on SS 316 substrates
Substrates of SS304, 316 and Carbon steel (1-inch diameter) were coated with a first layer of TiN using cathodic arc technique, followed by a second layer of ZrO₂ deposited by laser ablation deposition. Fig. 4 shows the SEM micrographs of TiN coating on SS316 and ZrO₂ coated on top of TiN coating. As can be seen from the figure, the coating is uniform and homogenous. Surface analysis using EDXA indicates surface elemental composition of the coated samples showing peaks of Ti and Zr. Of importance is to also recognize the peaks of nitrogen and oxygen from TiN and ZrO₂.

Figure 5 shows SEM images of titanium nitride coatings on two different stainless steels deposited using two different methods, cathodic arc and magnetron sputtering. It is also clear that magnetron sputtering is capable of producing uniform coatings, which is one of the reasons it was chosen as the deposition technique in this research.

Figure 6 shows a fairly uniform coating thickness of roughly 235 nm over a portion of the surface of a SS304 disk. Using FIB imaging, TiN proved to be the thickest coating out of the five materials selected for the same deposition duration. The higher thickness for TiN is based on the fairly high sputtering yield of TiN compound targets. The TiO₂ coating on SS304, as shown in Fig. 7, has a coating thickness around 30 nm, which is roughly an order of magnitude thinner than the TiN coating. Each of the metal-oxide coatings proved to be less than 100 nm thick, owing to the very low sputtering yield of oxide targets. The extremely thin oxide coating layers make a good case for the use of reactive sputtering.
Gamma Attenuation of Coated Samples

Substrates SS304 and 316 with and without coatings were tested for their gamma attenuation using stacked Ba-133 (356 keV), Cs-137 (661.7 keV) and Co-60 (1173 keV and 1332.5 keV) sources. The detector is a 2” x 2” sodium iodide (NaI) scintillator, with built-in photomultiplier tube (PMT) and preamplifier, connected to a high voltage power supply, shaping amplifier, and multichannel analyzer (MCA). The three gamma sources are tested separately to avoid self-shielding. The detector is placed 60 cm directly
above the source, and the disks are placed one-third of the way between source and detector, assuring most photons reaching the detector pass through the disk. Figure 8 illustrates gamma attenuation measurements setup. Table 1 shows the results of the samples gamma ray mass attenuation coefficient. There isn’t essentially much difference between the mass attenuation coefficient of the bare substrates and the TiN coated ones showing a decrease in the mass attenuation coefficient with the increase in the photon energy. Samples with a second layer of ZrO$_2$ coating (on top of the TiN) have shown higher coefficient at all photon energies.

<table>
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<tr>
<th>Photon Energy (keV)</th>
<th>SS304 Bare Substrate $\mu/\rho$ (cm$^2$/g)</th>
<th>SS304 TiN Coated $\mu/\rho$ (cm$^2$/g)</th>
<th>SS304 TiN+ZrO$_2$ $\mu/\rho$ (cm$^2$/g)</th>
<th>SS316 Bare Substrate $\mu/\rho$ (cm$^2$/g)</th>
<th>SS316 TiN Coated $\mu/\rho$ (cm$^2$/g)</th>
<th>SS316 TiN+ZrO$_2$ $\mu/\rho$ (cm$^2$/g)</th>
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<td>356.012</td>
<td>0.0870</td>
<td>0.0890</td>
<td>0.1953</td>
<td>0.0784</td>
<td>0.0742</td>
<td>0.1170</td>
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<tr>
<td>661.657</td>
<td>0.0634</td>
<td>0.0281</td>
<td>0.1970</td>
<td>0.0644</td>
<td>0.0345</td>
<td>0.0822</td>
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<td>1173.22</td>
<td>0.0459</td>
<td>0.0259</td>
<td>0.2950</td>
<td>0.0550</td>
<td>0.0287</td>
<td>0.1029</td>
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<td>1332.49</td>
<td>0.0307</td>
<td>0.0458</td>
<td>0.3506</td>
<td>0.0526</td>
<td>0.0320</td>
<td>0.1107</td>
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Table 1 Measured gamma ray mass attenuation coefficient of coated samples

Fig. 8 Gamma attenuation experimental setup
Surface Hardness with 1.1MRad gamma exposure

Samples of substrates were exposed to gamma ray unit a Co-60 irradiation unit, a 2.44kRad/hr for 451 hours (~19 days) to complete cumulative exposure of 1.1MRad. Substrates were exposed to assess their change in the Vickers hardness to establish the baseline before testing coated substrates. Figure 9 shows the hardness test results, where surface hardness slightly drops after long term exposure for tested SS and carbon steel. Results are also compared to published data for annealed or heat-treated substrate materials.

![Hardness Chart](image)

**Fig. 9** Surface hardness of SS034, SS316 and A36 substrates exposed to a Co-60 gamma unit

Surface hardness of coated samples are measured prior to their exposure to gamma ray as shown in Fig. 10. Surface hardness of post exposure is shown in Table 2, showing a slight change in surface hardness.
Table 2: Surface hardness of samples exposed to 1.1 MRad gamma ray source

<table>
<thead>
<tr>
<th>TIN coated SS304</th>
<th>TiN Coated SS316</th>
<th>ZrO₂/TiN coated SS304</th>
<th>ZrO₂/TiN coated SS316</th>
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<td>199.22</td>
<td>192.43</td>
<td>178.6</td>
<td>187.12</td>
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Extended exposure of the coated samples up to 3.3 Mrad and 4.4 Mrad have shown no appreciable change in surface hardness as these coatings are thin within few micrometers.

**Neutron Attenuation**

Neutron attenuation measurements of the single layer coatings were obtained using a Cf-252 spontaneous fission source and a 2-inch diameter, 6-inch active length He-3 detector. Cf-252 emits neutrons of average energy 2.1 MeV with a spectrum similar to what would be emitted from spent fuel. Three 5-minute counts were recorded for each sample in three configurations: single disk, two disks stacked, and three disks stacked. Figure 11 depicts the experimental setup.
Neutron measurements showed no statistically significant change in average count rate between bare and coated samples. Figure 12 shows neutron attenuation for single, double and tribble layered samples with no significant changes. The steel substrates are 1.5 mm thick and coatings are approximately 1 µm thick. The mean free path (MFP) of fission neutrons in stainless steel is roughly 3.5 cm. The neutron MFP is over 20 times greater than the combined thickness of the steel substrate and coating.
Fig. 12 neutron attenuation for single, double and tribble layer coatings
Circulators in simulated concentrated water for corrosion under circulated flow

Samples of bare substrates and coated ones are under long term SCW circulation in the in-house built circulators, with solutions at different pH’s. They are submerged in the circulated SCW for as long as 150 days to assess their corrosion. Figure 13 shows the in-house built circulators, where piping is made from PVC and the pumps used are capable of circulating liquid at 1 gallon per minute. The mass of each sample is measured at regular intervals to determine the change in weight due to corrosion. The compositions of the corrosive solutions are made from composition that provides specific pH as simulated concentrated waters (SCW) meant to emulate ground water compositions that are present in Yucca Mountain.

![Fig. 13 Circulators flowing SWC with various pH’s for extended testing over 140 days](image)

<table>
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<th>pH = 2.4</th>
<th>pH = 8.2</th>
<th>pH = 13.15</th>
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<tr>
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<td>Quantity</td>
<td>Compound</td>
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<tr>
<td>H₂O</td>
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<tr>
<td>NaCl</td>
<td>70 g</td>
<td>KCl</td>
</tr>
<tr>
<td>KCl</td>
<td>70 g</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>KNO₃</td>
<td>15 g</td>
<td>NaCl</td>
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<tr>
<td>MgSO₄</td>
<td>15 g</td>
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<td>NaOH</td>
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<td>H₂SO₄</td>
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Table 3 Simulated concentrated water (SCW) solutions used in circulators
The solutions contain significant concentrations of chlorides and cover a wide pH range. Solution with 13.08 pH composed of 87g KCL/79g NaCl, 20mL NaOH and 660mL H₂O is in use for bare substrates (SS304, SS316 and Carbon steel 'CS') and the result for the weight change for 44 days show that there is no change. Solution with 0.31 pH composed of 70g KCL/70g NaCl, 6mL NaOH, 20mL H₂SO₄, 15g MgSO₄, 15g KNO₃ has shown slight weight loss of carbon steel substrates over 30 days of experimental run. This is due to the inclusion of H₂SO₄ and MgSO₄. Testing of SS304, SS316 and TiN coated SS316 using solution with 1.76 pH composed of 70g KCL, 15g KNO₃, 15g MgSO₄, 5mL H₂SO₄, 4mL NaOH and 1000mL H₂O has shown no appreciable change in the weight, which indicates that the coated sample has not suffered from circulatory corrosive SCW.

Three SCW with 2.4, 8.2 and 13.15 pH have been used for a 140 days corrosion tests. The composition of these SCW’s is show in Table 3.

Bare and coated stainless steel samples showed no measurable weight change over a full 140-day period in any of the three solutions. More importantly, the coatings were still intact following extended submersion. This confirms good corrosion resistance and adhesion of the protective coatings. Carbon steel samples saw measurable corrosion in all solutions, with up to 3% weight loss after almost 5 months. Corrosion in the low pH solution was highest, as sulfuric acid makes for an aggressive solution. It is expected that carbon steel will experience measurable corrosion, especially in acidic conditions. Figure 14 shows graphs of measured mass over time for four coated steels in each of the three SCW solutions. Mass remains nearly unchanged for all but the carbon steels in the acidic solution. Coated and bare steels show the same trends.
Simulation of particle impact on protective coatings

The simulation of particle impact of the coated layers was conducted using the open source codes SRIM (Stopping and Range of Ions in Matter) and TRIM (Transport of Ions in Matter) to provide detailed assessment of the interaction of ions, and heavy particles, with matter including the range, backscattering, ionization, transport, vacancies, damage, projected straggle and sputtering (Ziegler et al. 2008; Ziegler et al. 2010; Ziegler and Biersack 2009). The configuration used for simulation is illustrated in Fig. 15 for multilayers, and for synthesized single blended layer as shown in Fig. 16.

![Fig. 15 Schematic of the multi-layer multi-component coatings](image1)

![Fig. 16 Schematic of the synthesized nanocrystalline single-layer coating](image2)
An assumed 1mm radius micro crack in the canister wall, and allowing 5000 heavy particles (monoenergetic fission neutrons) with an average of 1-2MeV energy to pass through, the energy fluence passing through the micro crack (1mm radius) into the first coating would be 255 to 509J/m² for the energy range of 1 to 2 MeV, respectively. For each case, the particles are monoenergetic with fixed energy of 0.5, 1, 1.5 or 2 MeV, so there is no distribution as the simulation is not for particles with different energies. At particle energy of 2.0MeV, the damage occurs deeper into the first layer (TiCN) at almost its full thickness of 10mm as shown in Fig. 17 and similarly in the composited coating with a few tracks extended through the full length. Simulation results indicate that an increase in the thickness of the first layer (TiCN) is preferable to limit the damage within this layer. While one can see that the distribution of the damage, as seen from particle tracks into the coating as a cluster around the point of attack, however, scattered particles are reflected back from the surface as a fraction of the incident monoenergetic particles. It was determined that coating in the layered and composited structures can perform almost similarly in terms of surface damage, penetrability, and vacancies per incident particle, but slightly different for the backscattering.

![Fig. 17 Heavy particle track in 3-layers (left) and composited (right) at 2.0MeV proton energy](image)

**Cyclic polarization and corrosion rates**

Cyclic polarization test of substrates at elevated temperature was performed for SS304 and SS316 substrates. The cyclic polarization curves indicate increased corrosion rate with increased temperature. Electrochemical testing technique was conducted using the MULTIPORT™ corrosion cell kit and Interface 1000 from Gamry Instruments, along with the DC105 electrochem software. A standard three electrode setup with a graphite counter electrode and saturated Ag/AgCl reference electrode is used. The reference electrode is placed directly in the corrosion cell to avoid problems posed by a salt bridge. The samples are placed in a holder conducive to testing disks of vary thickness, such that the total exposed surface area to the aerated 1 M NaCl solution is 4.15 cm². Figure 18 shows a photo of the experimental test cell and the associated instrumentation. Figure 19 shows the details of the electrochemical corrosion test cell
inside a water bath with controlled temperature up to 95°C to evaluate corrosion at elevated temperature.

![Corrosion test cell with associated instrumentation](image)

Figure 18 Corrosion test cell with associated instrumentation

![Electrochemical polarization setup in a temperature controlled water bath](image)

Fig. 19 Electrochemical polarization setup in a temperature controlled water bath
Cyclic polarization of ZrO$_2$/SS316, TiO$_2$/SS304 and TiN/A36 are shown in Fig. 20 at elevated temperatures from room temperature ($20^\circ$C) to 40, 60 and 80$^\circ$C. The capacity for passivation can be determined from cyclic polarization curves, as shown in Fig. 20. The passive region is defined by a small change in current over a large potential range, which corresponds to a near-vertical line on the polarization curves. The shape of the cyclic polarization curves is very similar for all coatings. This suggests that the corrosion of all samples is influenced by the steel substrate regardless of the coating material. The A36 steel exhibits no discernible passivity because it corrodes uniformly at a much higher rate than stainless steel. Most iron oxide films that form on the surface are readily dissolved by corrosion on the surface of the metal. Iron (and low-alloy steels) is capable of passivating at in certain environments at very high critical current densities ($\sim 1-10$ A/cm$^2$), though current above 1 A cannot be measured by the potentiostat in use, so current densities were kept well below the supposed critical values for iron. Thus, no passive behavior was observed for A36 mild steel.
Fig. 20 Cyclic polarization curves for coated samples at temperatures from 20 to 80°C
The average corrosion current density versus temperature is plotted in Fig. 21 for bare and singly-coated steels in 1 M NaCl. The corrosion current density increases exponentially with temperature and can be described by the equation

\[ i_{\text{corr}} = A \cdot \exp \left( -\frac{E_a^0}{RT} \right) \]

where \( i_{\text{corr}} \) is the corrosion current density (\( \mu A/cm^2 \)), \( A \) is the pre-exponential factor (\( \mu A/cm^2 \)), and \( E_a^0 \) is the apparent activation energy (kJ/mol). It is also possible to use the Eyring’s equation

\[ i_{\text{corr}} = \frac{RT}{N_a h} \exp \left( \frac{\Delta S_a^0}{R} \right) \exp \left( -\frac{\Delta H_a^0}{RT} \right) \]

where \( N_a \) is Avogadro’s number (= 6.022e23 mol\(^{-1}\)), \( h \) is Planck’s constant (= 6.626e-34 J\(-s\)), And \( \Delta S_a^0 \) and \( \Delta H_a^0 \) are the entropy and enthalpy of activation, respectively.
Fig. 21 Average corrosion current density vs. temperature for coated SS304, SS316 and A36
Compressive Peeling Tests

Compression test stand (Mark-10 TSA750 Lever Operated Manual Test Stands, 750 lb, Vertical; with Mark-10 TSA001 Digital Travel Display) has been used to test compression and peeling of the coated samples. Figure 22 shows the test stand, where sample will be placed between the compressing grips and up to 2500 N of force will be applied. Samples placed horizontal with the compressing pointers at the middle of the sample will show the effect of the load and if the coating would peel or flake. Sample placed vertical will show when the compression will deform the coating and peel it off. Test results of coated samples have shown no delamination or peeling of flaking up to 2500 N force, indicating good adhesion of the coating on the substrates.

A new design of a stress corrosion unit was in-house manufactured to test stressing samples while immersed in SCW's with various pHs to test corrosion under simulated conditions; this test stand will be used in future evaluation of coated samples on steel substrates.

Fig. 22 Compression test stand fully assembled with grips and digital display (left) and details of the stand structure (middle), and new in-house built test stand for stress corrosion with samples immersed in brines at different pHs.
6. PRODUCTS DEVELOPED
6a. Publications

Peer-reviewed Journal Articles


“Corrosion of Single Layer Thin Film Protective Coatings on Steel Substrates for High Level Waste Containers”, Michael A. Fusco, Yasar Ay, Abigail H. M. Casey, Mohamed A. Bourham and A. Leigh Winfrey, Progress in Nuclear Energy, Vol. 89, pp. 159-169, February 2016


Conference Presentations
“Evaluation of Coated Barrier Materials on Steel Substrates for Spent Nuclear Fuel Storage Applications”, Michael Fusco, Yasar Ay, John Echols, Abigail Casey, Kathryn Tuason, Sean Kerrigan, Jordan Schweigert, Caroline Campbell, Mohamed Bourham and Leigh Winfrey, UNC Charlotte Graduate Research Symposium, Charlotte, NC, 11 April 2015

"Fabrication and Characterization of Magnetron Sputtered Zirconium Dioxide Thin Films on Steel Substrates", Sean P. Kerrigan, Caroline A. Campbell, Jordan Schweigert, Michael Fusco, Yasar Ay, Mohamed Bourham, A. L. Winfrey, Abigail H.M. Casey, and J. R. Echols. Student ANSI Summary (2015), College Station, TX, Texas A&M University, April 9-11, 2015

