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Passivation of Stainless Steel for Tritium Service

R.B. Wyrwas
P.S. Korkinko

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REVIEWS AND APPROVALS

AUTHORS:

R.B. Wyrwas, Immobilization Technology, Waste Form Processing	Date
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P.S. Korkinko, Energy Materials Programs, Renewable Energy Programs	Date
---	------

TECHNICAL REVIEW:

B. Peters, Energy Materials Programs, Renewable Energy Programs	Date
---	------

APPROVAL:

B. L. Garcia-Diaz, Manager Energy Materials Programs, Renewable Energy Programs	Date
--	------

PREFACE OR ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

The goal of this project was to develop a method to passivate stainless steel components using electropolishing techniques and heat treatment methods. The process is intended to limit the ingrowth and isotope exchange of hydrogen with tritium and deuterium as well as other undesired contaminants of standard gas mixtures. This process has been named Q-Passivation, to set it apart from standard industrial passivation methods and a patent application has been submitted and published on the process. The basis used for the development of this process was taken from the surface analytical data collected from decommissioned commercial tritium containment vessels that are used to hold standard gas mixtures. The information gained from the surface analysis along with the methods to eliminate residual hydrogen contamination will provide a reasonable method for passivation. Barriers in fabricating test vessels for tritium have delayed production for tritium exposure trials. Some of these barriers include base metal composition that may meet compositional specifications but does not meet a quality inspection as it contains inclusions, additional phases, and other metallurgical anomalies. A number of issues and challenges were encountered during this project that should be resolved. These challenges include base material specification, a non-destructive quality assurance technique, the use of other materials aside from 304L stainless steel, and reuse of expired standard gas containers.

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LIST OF ABBREVIATIONS

AES	Auger Electron Spectroscopy
CrEEP	Chromium Enriched Electropolishing
CTCV	Commercial Tritium Containment Vessel
EDS	Energy Dispersive X-Ray Spectroscopy
HP	Harsh Polish
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LIBS	Laser Induced Breakdown Spectroscopy
NDE	Non-Destructive Evaluation
NSE	Nuclear Security Enterprise
Ox	Oxidation Heat Treatment
SEM	Scanning Electron Microscopy
SRTE	Savannah River Tritium Enterprise
VEx	Vacuum Extraction
XPS	X-ray Photoelectron Spectroscopy

1.0 Introduction

Savannah River Tritium Enterprise (SRTE) no longer has a reliable source of passivated stainless steel components to meet the facility needs; the prior vendor has not been able to supply the quality components required and has lost technical resources to troubleshoot defective products. The Nuclear Security Enterprise (NSE) uses gas standards bottles for calibration and transport purposes. If the gas standards change composition with time due to hydrogen off-gassing or catalytic reactions with surfaces, this will impact the ability to qualify instrumentation and products, which in turn may cause process delays or could compromise the end product.

This project was initiated in FY 2016 with the goal of determining the methods and specification requirements for passivation of stainless steel standard commercial tritium containment vessels (CTCV) and gas manifold components. Standard passivation methods for stainless steels are generally one-step processes that typically involve chemical or electrochemical preparation of the surface.¹ These processes are not adequate to limit hydrogen ingrowth and isotope exchange in tritium gas standards and eliminate catalytic formation of hydrogen containing species. Market surveys of vessels treated by these processes have found an ineffectiveness in recently procured bottles and bottles that were commercially “passivated”.²⁻⁵ In these surveys, containers that were treated by electrochemical or chemical passivation methods alone did not adequately build a substantial chromium and oxygen enriched surface that resulted in an effective barrier and did not limit hydrogen ingrowth into the system as the properly processed sole source vendor-supplied vessels can achieve. When preparing tritium containing vessels, a second step is needed to adequately prepare an inert surface. Hence forth, we will refer to this process as “Q-passivation” to set the passivation process apart from industrial passivation processes which are used for corrosion control and general material performance. Literature studies and forensic analysis of decommissioned CTCVs that were found to perform as expected and others that failed the qualification have indicated that a surface layer of chromium oxide is required for effective Q-passivation.

The work presented by Peebles⁵ showed that the oxygen enriched layer need to be on the order of 100 nm for an acceptable barrier. Figure 1 shows the results from x-ray photoelectron depth profile analysis which shows the relative concentration of a specific element as a function of depth. The results indicate several layers of oxygen-rich material are present along with a thin layer of chromium oxide at the surface. An accompanying profile for iron (not shown) exhibits little to no iron oxide present.⁶ A similar issue exists in vacuum technology when trying to limit the degassing of permeated hydrogen in ultra-high vacuum systems. A common technique that exists for the passivation of vacuum chamber surfaces involves a two-step process of electropolishing followed by a vacuum heat treatment.⁷ The resulting oxygen enriched layer inhibits the migration of H₂ that is liberated from the bulk stainless steel into the vacuum chamber and it also limits surface capture by diminishing catalytic metal centers on the surface that capture hydrogen and water.

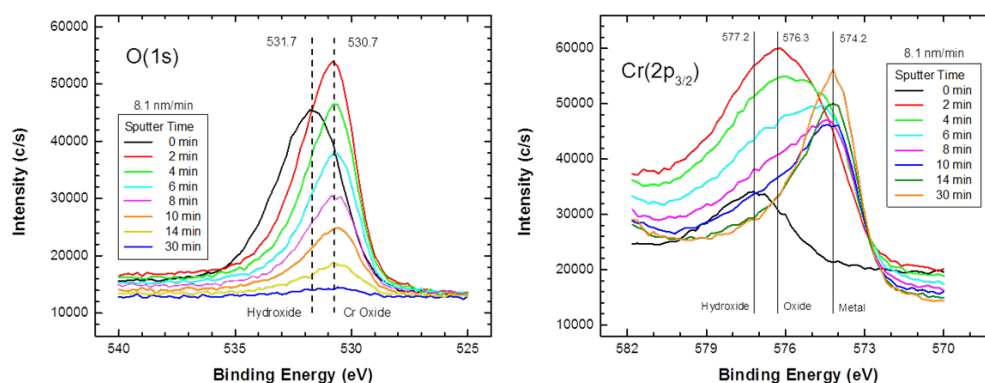


Figure 1. X-ray Photoelectron Spectroscopy depth profiles for oxygen and chromium of a passivated bottle that performed as specified.

The goal of this project was to develop a surface treatment method that limits the ingrowth of H_2 and exchange products with other isotopes. The surface treatment will need to restrict outgassing from treated components and eliminate chemical reactions that produce undesired species, such as ammonia and methane.

2.0 Development Q-Passivation

2.1 Overview of Development

The goal of this project is to render type 304L surfaces inert to hydrogen isotopes much like the goals of chemical passivation, or corrosion passivation, which render surfaces less reactive to the specific environment of concern. This process used two techniques to accomplish this: electropolishing and vacuum heat treatment. As stated above, the term “Q-passivation” has been conceived to differentiate the general term of passivation from what is required for the tritium facility, where “Q” is used as a substitute for the hydrogen isotopes (e.g., Q= H, D, or T in water, ammonia or methane).

A significant amount of progress towards developing the Q-Passivation method on Type 304L Stainless Steel¹ coupons has been completed since this project’s inception.⁸ It has been determined that high voltage polishing results in uniform material removal which was substantiated using ICP-MS of the chemical solutions after what is termed Harsh Polish (HP). This step leaves the coupons with a mirror finish effectively minimizing the surface area by reducing surface roughness. A second electropolishing step at lower voltage resulted in a chromium enriched surface (CrEEP – Chromium Enriched ElectroPolishing) was developed; these conditions were also established based on ICP-MS data of the solutions and substantiated by Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS). A method to reduce the hydrogen background and a control system to ensure that the pressures did not exceed high vacuum conditions during heating was also developed; this process is termed Vacuum Extraction (VEx). A vacuum oven with a programmable heater and software that regulated the power to the heating elements before the pressure exceeds 1×10^{-6} Torr was built and used especially for this process; this pressure limit was defined by Sasaki.⁷ This step removes the nascent hydrogen produced during electropolishing as well as the hydrogen present in the base material. An oxidation heat treatment has also

¹ 304L stainless steel nominally contains 17.5% to 19.5% Chromium, 8% to 12% Nickel, and less than 0.03% carbon.

been developed that results in a light yellow to gold heat tint (optically transparent oxide film) to form on the surface of the electropolished stainless steel, in a process simply termed Ox. These terms allow identification of the samples after each major processing step. A sample that has been fully processed is shown in Figure 2 and the surface analysis results for samples that were partially and fully treated are shown in Figure 3, with EP, CrEEP, and Vex (VT), represented in Figure 3A, and EP, CrEEP, Vex(VT), and Ox (HT), represented in Figure 3B. Additional development of the oxidation process provided the ability to obtain a thicker oxide that ideally precludes iron oxide formation. The base metal is reached after sufficient sputter time as observed by the steady compositions. For example, the results after sputtering for 1 minute in Figure 3A show the base metal composition.

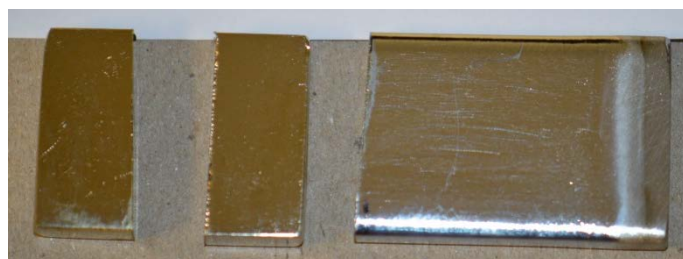


Figure 2. Image showing a sample that has been electropolished, vacuum extracted (right), and mildly oxidized at 300 (middle) and 350°C (left).

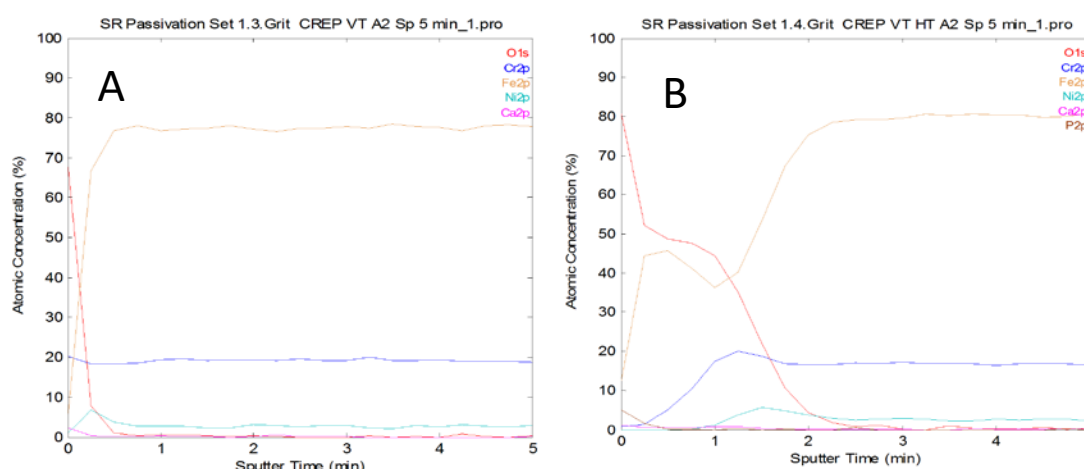


Figure 3. X-ray Photoelectron Spectroscopy depth profile results after A) partial and B) full processing.

2.2 Development of Electropolishing Methods:

Reduction of the surface roughness decreases out-gassing and surface reactivity of stainless steel, by reducing the atomic surface area available for adsorption and catalytic processes. In addition to the reduction of surface features, under the correct electropolishing parameters, specific elements can be targeted for preferential removal from the stainless steel. The oxidation potential for chrome and chrome oxide is higher than that of iron and nickel. By using a lower potential (voltage) below the chrome potential but above the iron and nickel potential, nickel and iron can be selectively removed from the surface of the stainless steel leaving a chromium enriched surface layer. The reduction in surface asperities followed by the removal of Ni and Fe is the goal of the electropolishing treatments and can be accomplished through the refinement of several variables. A partial factorial experimental matrix was used to study the following

variables: sulfuric/phosphoric acid electropolishing bath composition, time, current, and acid bath temperature. After electropolishing, samples were examined by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Auger electron spectroscopy (AES) [or X-ray Photoelectron Spectroscopy (XPS)], and laser induced breakdown spectroscopy (LIBS). Additionally, inductively coupled plasma – mass spectrometry (ICP-MS) was used to characterize the elemental content of the acid solution post electropolishing.

A range of electropolishing conditions were tested to evaluate the impact of acid composition, current density, polishing time, and acid bath temperature as listed in Table 1. The electropolishing (EP) conditions resulted in two different visually distinct surfaces, a smooth, mirrored finish and frosted gray finish. The SEM images in Figure 4(a-d), show an example of each surface type. Chemical analysis (EDS) of the electropolished coupons did not show any increase in chromium content and was consistent with the bulk composition; this result is due to the penetration depth of the electron beam and the energy of the observed electrons. Auger electron spectroscopic depth profile analysis was performed on all nine of the samples. Three trends were observed, an increase in the Cr, a decrease in the Cr, and no apparent change in the Cr. AES data for each type of behavior is shown in Figure 5. Sample 3-3 (1000 mA/cm² at 70 °C, acid ratio 60:40, Figure 4B and D) resulted in a rough finish and exhibits a reduction in Cr at the surface and a gradual increase to bulk content. Sample 4-1 exhibited a smooth finish (10 mA/cm² at 50 °C, acid ratio 50:50, Figure 4A and C) indicates an increase of the surface Cr while sample 10 (1000 mA/cm² at 50 °C, acid ratio 70:30) has a steeper slope for the Cr concentration.

Table 1. Parameters for electropolishing test matrix.

Variables	Values		
Acid Ratio (H ₂ SO ₄ :H ₃ PO ₄) {H}	60:40	50:50	70:30
Current Density (mA/cm ²) {i}	10	100	1000
Temperature (°C) {T}	30	55	70
Time (min) {t}	2	10	20
Code	1	2	3

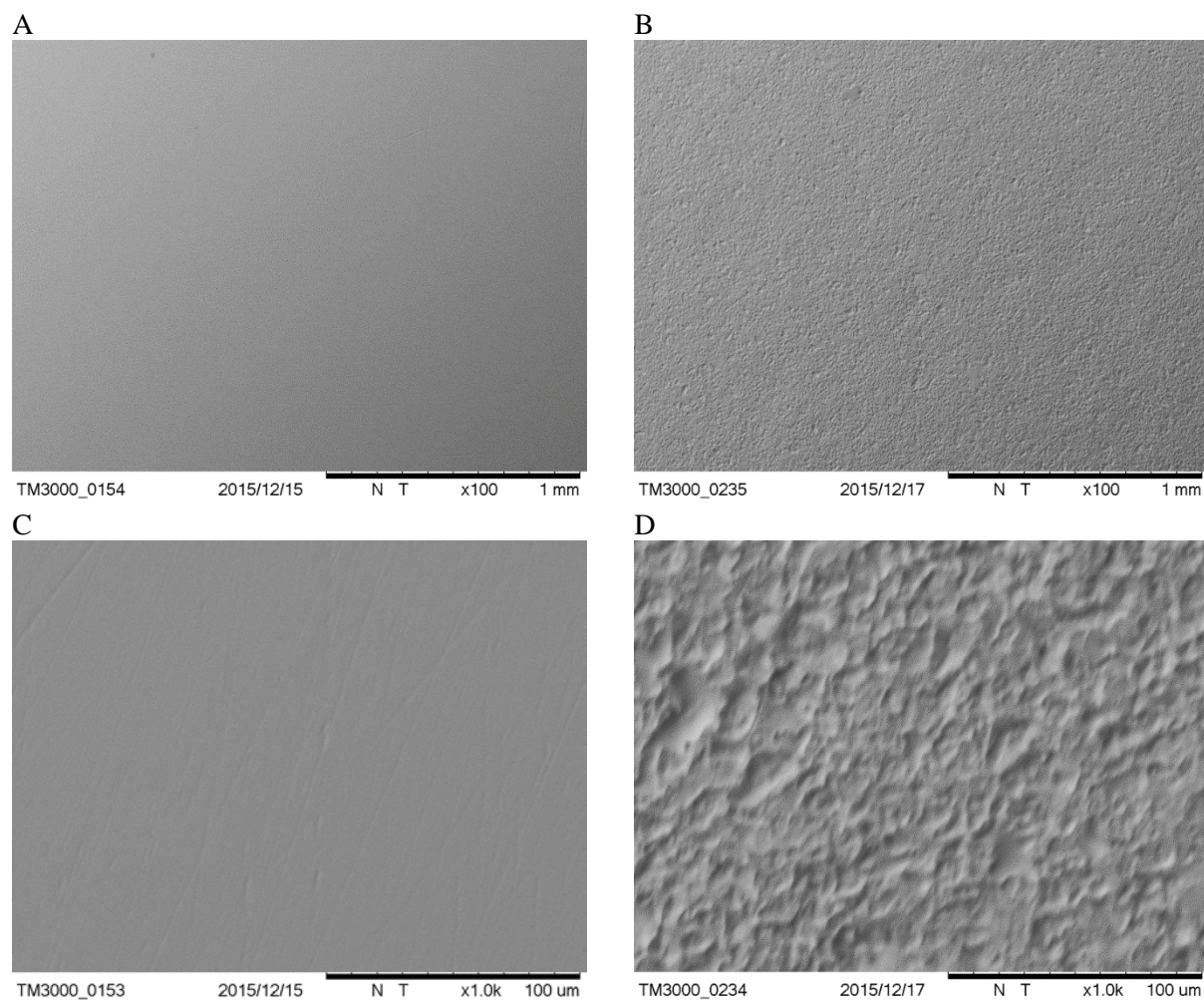
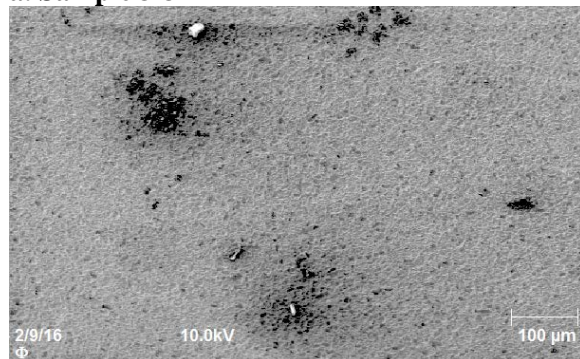
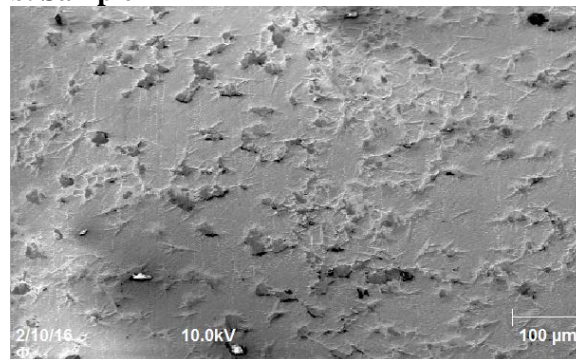


Figure 4. Example of electropolished coupon results, (a) smoothed result, 100x (b) rough, frosted result, 100x, (c) smoothed result, 1000x, (d) rough, frosted result, 1000x.

a. Sample 3-3



b. Sample 4-2



c. Sample 10

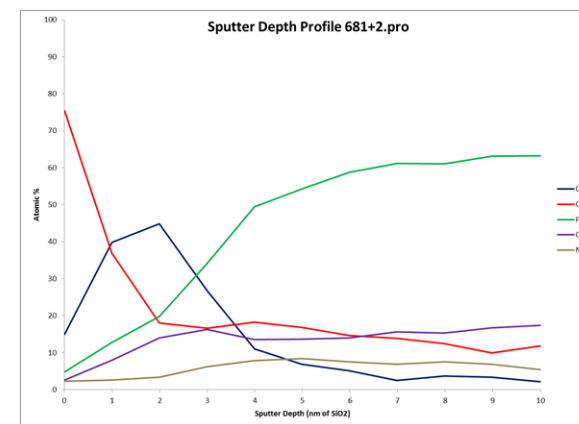
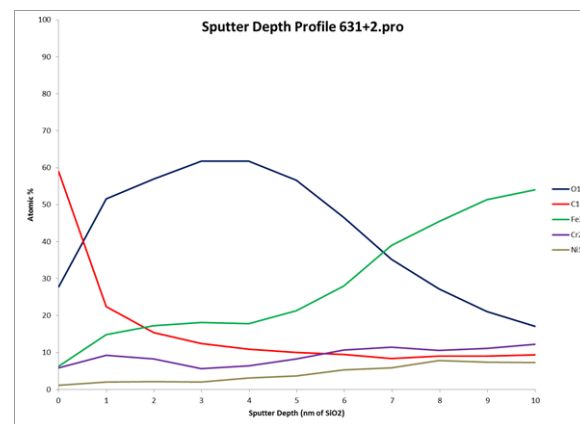
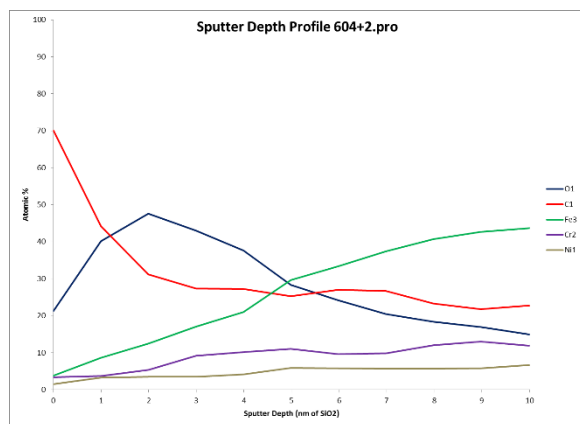
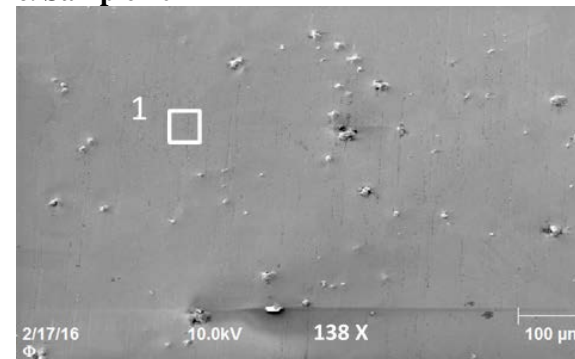


Figure 5. SEM image and AES depth profile from sample 3-3 (a) sample 4-2 (b) and sample 10 (c) from the statistically designed experiment.

Laser induced breakdown spectroscopy (LIBS) was suggested as a rapid analysis tool for determining the elemental content of the surface. The spectra presented in Figure 6 shows the LIBS data for three laser shots for each of the samples shown in Figure 2. Using Atomic Force Microscopy, it was estimated that each laser shot ablates the surface approximately 150 nm therefore multiple shots can produce a 3-point depth profile of the material. The data indicate similar trends to those observed by AES, although the depth of penetration for each shot is significantly greater than that observed in AES. In addition, the benefit of LIBS data is that it can be captured and analyzed in significantly less time than it took to obtain the AES data with virtually no sample preparation. While this technique is not refined enough to provide quantitative results, the qualitative data is expected to be useful to determine the relative amounts of Cr, Ni, and Fe at and near the surface.

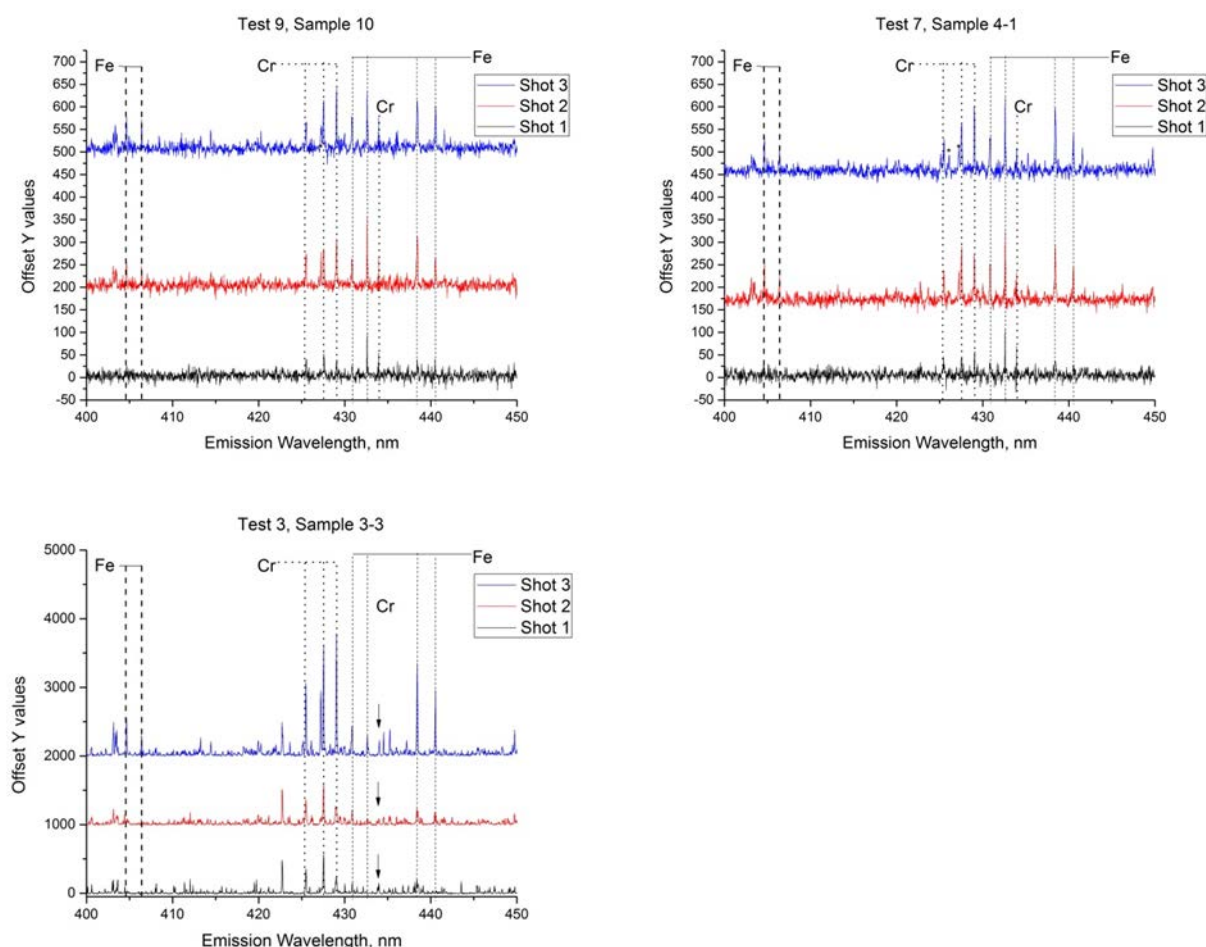


Figure 6. LIBS spectra of EP sample 3-3 (a) sample 4-2 (b) and sample 10 (c) from the test matrix.

Chemical analysis, using inductively coupled plasma mass spectrometry (ICP-MS) of the polishing solution after each sample was polished was performed and it was determined for the all the conditions tested the resulting composition of Cr, Fe, and Ni in each solution was similar to that of the composition of the base metal. Although there were subtle differences in the surface chemistry measured in the Auger depth profile, no set of conditions stood out to be remarkable or appeared to be the best set of conditions for this process. Based on the analysis for the oxygen depth, maximum oxygen content, and chromium content, high

temperature (70°C) and 10 mins of polishing time give the maximum thickness and content. The 60:40 sulfuric acid to phosphoric acid was found to provide greater chrome content, but the 50:50 mixture provides the best surface finish. Determining the optimum current density was not as straight forward, while the higher current densities show promise to produce a thicker oxide, it is very aggressive and does not yield much chrome enhancement. Instead, the surface and polishing bath compositions indicate an equal removal of all elements of the base metal, i.e., the compositions are the same as the base 304L stainless steel. However, the test matrix results indicate that the lower current density will increase the chromium content.

Although elemental depth profile analysis from AES provides the most direct comparison to the forensic evaluation of the previous bottles, other characterization techniques were deployed to guide decision making and possibly lead to an in-process monitoring technique. Based on the ICP-MS data, it was determined that two separate sets of electropolishing conditions could provide an enhanced or polished surface and an increased chromium content. The first step is a harsh electropolishing (HP), necessary to decrease the surface roughness, while a second less aggressive set of conditions is used to preferentially remove Fe and Ni, thus leaving a Cr enriched layer. Figure 7 gives the results of the elemental percentage of chromium, nickel, and iron in the polishing solution determined by ICP-MS of the spent acid bath at different polishing voltages. The low abundance of chromium present in solution at potentials less than 2 V suggested that the base metal coupon still contains a high amount of chromium at the surface. In comparison to HP, the chromium enrichment electropolishing step (CrEEP) is very slow; where the HP step can be performed in 10 mins, the CrEEP step can take 16 hours or longer. The solution analysis was used to determine that the Cr enrichment could be achieved at 600 mV with respect to a silver:silver chloride reference electrode with a minimum polish time of 16hrs.

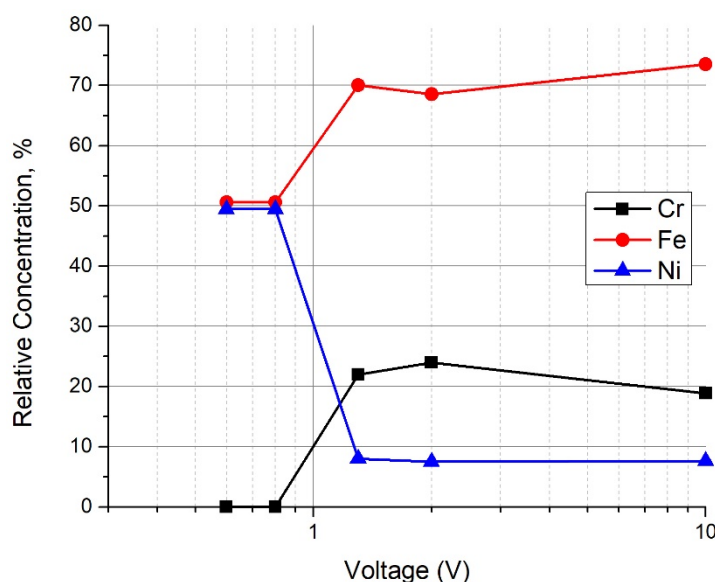


Figure 7. The percent abundance of chromium, nickel, and iron present in the polishing bath after the electropolishing versus polishing voltage.

2.3 Develop a vacuum heat treatment process:

Two different heat treatments are necessary to provide a Q-passivated surface: 1) vacuum heat treatment and 2) an oxidation step. The vacuum heat treatment is performed under controlled temperature/vacuum conditions. For this process a vacuum oven system was constructed with a pressure feed-back loop, which when coupled with the temperature controller, will maintain a heating profile to keep the total vacuum

pressure below 1×10^{-6} torr until a target temperature of 350°C is achieved.^a As the total pressure in the vacuum chamber increases with heating, the partial pressure of hydrogen increases via liberation from the steel into the vacuum chamber, which is then swept away by the vacuum system. Figure 8 shows the partial pressure profiles (left y-axis) overlaid with the total pressure (right y-axis) for an 86.5 hr hydrogen extraction run. It can be noted that a major fraction of the total pressure contribution is from the partial pressure of hydrogen (the partial pressure scale on the left axis is multiplied to about $\frac{1}{4}$ of the total pressure on the right axis.) The partial pressure was monitored using a residual gas analyzer, i.e., quadrupole mass spectrometer. After the 350°C target temperature is met, the temperature is maintained until the total vacuum pressure returns to the baseline pressure, $\sim 1 \times 10^{-8}$ torr, near the initial pressure after a 12 hour evacuation at room temperature.

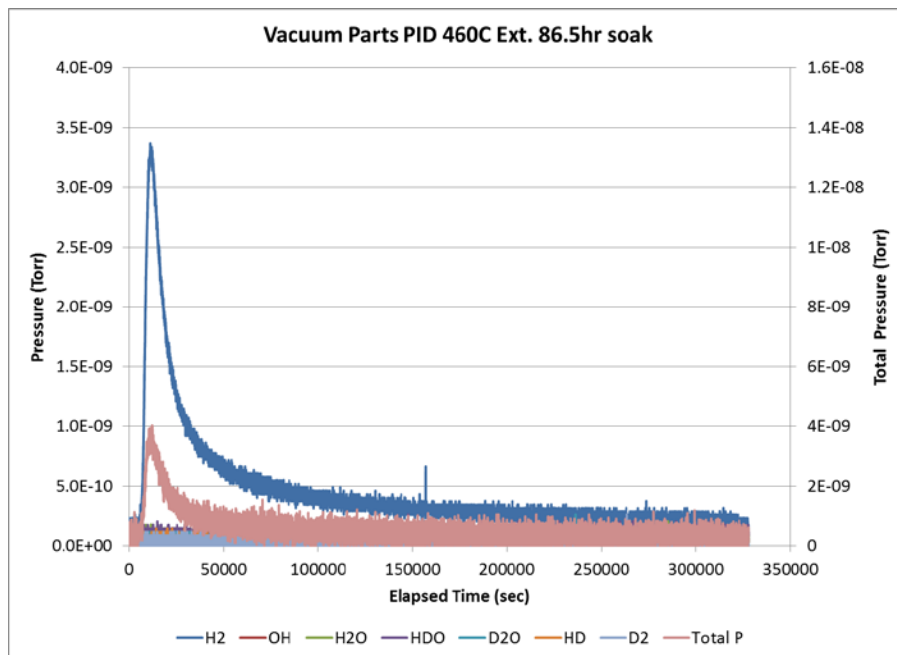


Figure 8. Hydrogen pressure profile compare to the total pressure profile over the duration of an 86.5 hr vacuum extraction for a run that was conducted using a $5^{\circ}\text{C}/\text{min}$ heating rate to 350°C .

Vacuum extracted samples have not shown significant surface oxide enrichment. Despite what thermodynamic data indicates, the low amount of oxygen in the vacuum extraction furnace is not an ample supply to allow sufficient oxidation to occur. For this reason, a controlled atmosphere oxidation furnace was assembled to allow controlled oxidation of the stainless steel surface at elevated temperature. A test matrix was developed to determine the most effective time, temperature, and gas composition for the oxidation of the surface. Figure 9 shows the XPS profile for a Q-passivated stainless steel sample compared to an untreated sample. Each spectrum is collected in 2-nm increments. For the Q-passivated sample that has undergone all 4 steps (right), the chromium oxide peak is approximately equal to the metallic chromium peak at 14 nm. Whereas in the untreated sample, below the surface only metallic chromium exists. This shows the effectiveness of the process as a whole. This can be observed by the shift in binding energy as the oxidation state of the chromium changes from oxidized to metallic with increasing depth.

^a Temperatures above 350°C could cause phase changes within the stainless steel that could compromise the integrity of a CTTV and disqualify the container as a transportation vessel, thus we have limited the process to this temperature.

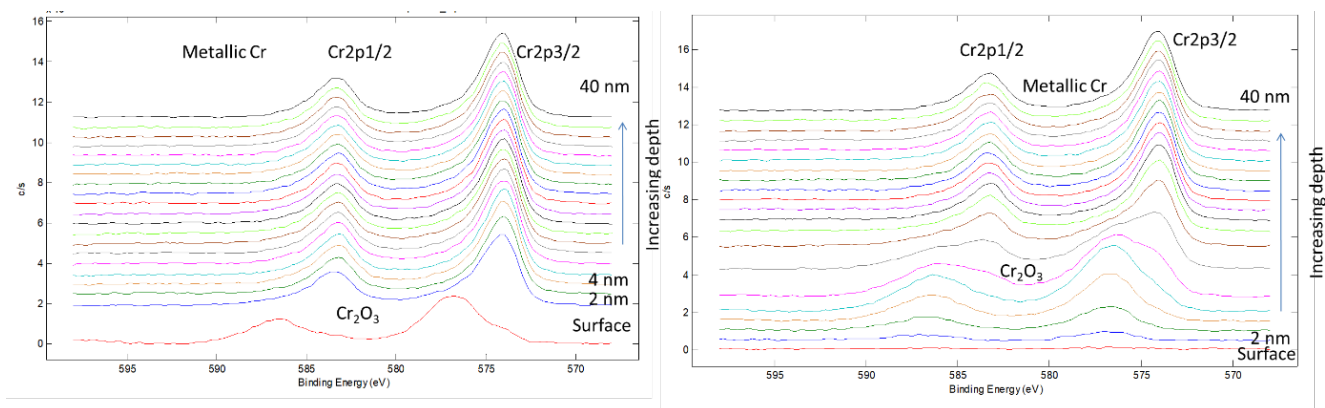


Figure 9. XPS depth profile of Q-passivated stainless coupons before (left) and after (right) oxidation. In the untreated sample the oxide layer is only 2nm deep while the oxide layer in the treated sample is approximately 16 nm deep. This data was collected and analyzed by Sandia National Laboratory.

3.0 Application of Q-Passivation Methods

Previous work used hydrogen isotope exchange methods (protium, deuterium, and tritium) to validate the robustness of passivated vessels for gas storage.¹⁻⁴ It is logical to use this as the next method to validate the Q-Passivation method outlined in Section 2. Processing of vessels in the laboratory poses some challenges as the shape and size of the vessel and components are much larger than the coupons used in the scoping study. Additionally, not all the areas of the completed vessel are accessible for inspection due to the shapes of the vessel. Since vessel geometry and access is limited, the electropolishing techniques had to be adapted to optimize the effectiveness of each step.

A simple test vessel assembly can be passivated for testing. An example of a vessel is shown in Figure 10 that consists of a 6" pipe nipple with 2.75" Conflat end caps, where one end cap has a valve stem attached. The conflat flange is commonly used in vacuum systems and components were procured from several vacuum supply companies; all of the vacuum components met the specification for Type 304L SS. Figure 11 shows a comparison of two Conflat flanges polished under harsh electropolishing conditions. In some cases, Conflat flanges polished as expected leaving a mirrored finish while in other cases the flanges resulted in the matte finish. Subtle differences in base material caused the flange on the right panel to have a rough matte finish. The SEM image in Figure 12 shows the surface of a Conflat flange before electropolishing. The electron dispersive spectrum on the of Figure 12 shows the composition of dark region under the yellow dot is almost entirely carbon. Visually similar regions on the flange had the same composition.



Figure 10. Conflat containment vessel, overall length is 10.5" (267 mm).



Figure 11. Electropolished Conflat flanges showing the variation in the base 304 L stainless steel.

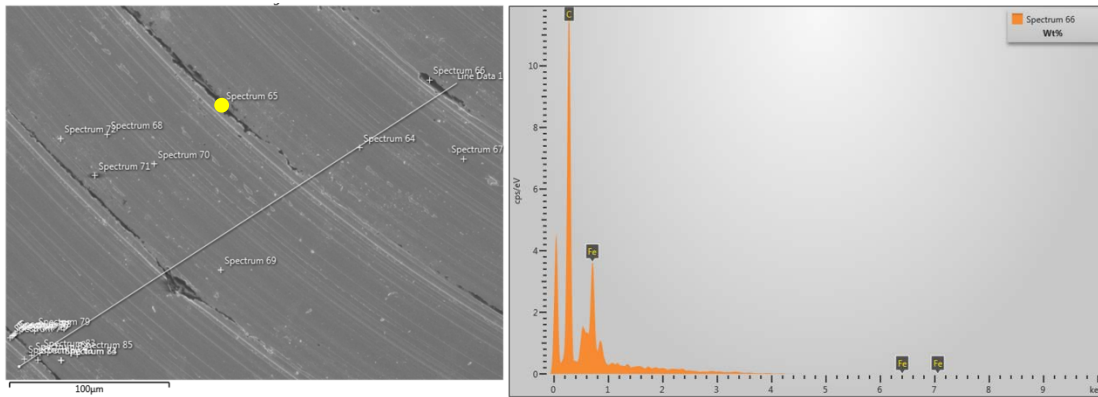


Figure 12. SEM image of a Conflat flange show surface condition prior to electropolishing. Energy dispersive spectrum of the point indicated by the yellow dot.

Surface contamination of differing composition was found on a number of components. A rigorous pretreatment surface cleaning step with a mixture of hydrofluoric acid and nitric acid was adopted to remove residue, surface oxides, and other chemical anomalies before electropolishing.

However, problems with the various sources of 304L stainless steel available to the manufacturing industry persisted. Figure 13 shows metallographic analysis of a cross-section taken from a Conflat blank purchased from a reputable vacuum component vendor. Figure 13A represents the face of the flange showing the grain structure and a number of dark colored inclusions. Figure 13B show the axial view of the flange cross-section in which the grain structure can be observed and the inclusions appear elongated in the axial

direction. After inquiries to machine shops and vacuum part vendors, it was confirmed that these parts were machined from bar stock that was drawn axially yielding the inclusions that were seen throughout the piece. It was later verified that historically Conflat vacuum flanges were machined from plate stock to alleviate perceived porosity issues found in some stainless steel.⁹ The perception would be due to interconnected stringers that are observed in Figure 13B.

The quality of the stainless steel is an issue for this process. Although the purchased components appear to have met the general industrial specifications for 304L stainless steel, there appears to be an allowable level of impurities found in these specimens that compromises the effectiveness of the electropolishing.

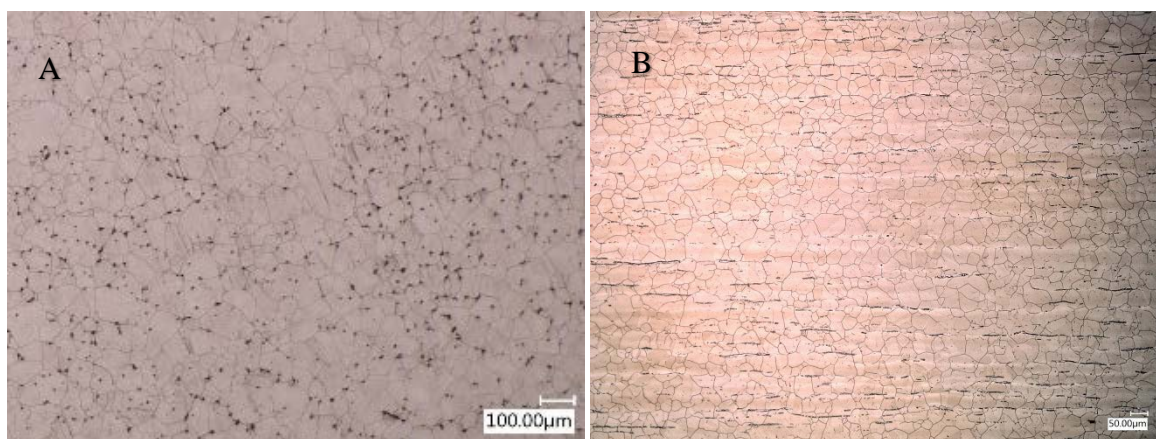


Figure 13. Microstructure analysis of Conflat flange that yielded major defects during electropolishing.

4.0 Summary

The goal of this project was to develop a method to passivate stainless steel components using electropolishing techniques and heat treatment methods. The process is intended to limit the ingrowth and isotope exchange of hydrogen with tritium and deuterium as well as other contaminants of standard gas mixtures. This process has been named Q-Passivation, to set it apart from standard industrial passivation methods and a patent application has been submitted and published on the process.¹⁰ The basis used for the development of this process was taken from the surface analytical data collected from decommissioned commercial tritium containment vessels that are used to hold standard gas mixtures. The information gained from the surface analysis along with the methods to eliminate residual hydrogen contamination will provide a reasonable method for passivation. Barriers to fabricating test vessels for tritium have delayed production for tritium exposure trials. Some of these barriers include base metal composition that may meet the compositional specification but does not meet a quality inspection as it contains inclusions and stringers. A number of issues and challenges were realized during the project that are suggested as future work for this area of need.

5.0 Recommendations, Path Forward or Future Work

This project has uncovered and discovered several potential issues unique to the passivation process and have recommendations for future work. This process lacks a quality assurance method that can investigate large volumes of the sample, much less the entire vessel or fabricated component. Auger spectroscopy coupled with sputtering depth profiling is the current method used to determine whether passivation performed by a vendor is adequate. This method is time consuming and can only interrogate a few very small areas and requires the vessel or component to be cut into pieces, i.e., the technique is destructive. Furthermore, this method can provide a false positive of acceptable treatment. Development of non-

destructive evaluation (NDE) is the focus of a project underway to investigate electrochemical methods that can be deployed in process to validate the electropolishing steps or final product. Isotope exchange methods using deuterium have been deployed in previous testing^{2,3} as an NDE method to determine Q-passivation performance. However, these methods are known to also provide a false-positive result as well, which leaves exposure to tritium as the best method for testing. A project is underway to investigate whether the isotope exchange reactions can be enhanced by adding other gas species to the mixture and probe the surface chemistry.

A base material specification should be established. Based on the difficulties encountered with industrial grade 304L, a better defined composition and microstructure is needed. The specification should limit the type and quantity of inclusions in the steel. Additionally, other facility needs may require passivation of alternate 300-series stainless steel alloy or higher alloys, such as those from the Inconel or Hastelloy families, which have wider compositional variations that may impact any of the passivation process steps and the performance of the component. The impact of these other metal elements (compositions) could impact the passivation surface treatment and introduce defects or expose potentially catalytic / reactive metals like titanium and niobium. Some preliminary work has been performed on 300-series and 400-series stainless steels and showed that process modifications may be required to for optimal performance.¹¹

There is a rising concern across the national security enterprise that tritium gas standards will fail to meet specifications because of poorly passivated gas standard bottles and the challenges associated with obtaining properly passivated bottles. Q-passivated tritium gas standard bottles are expected to hold a standard within specification for two years without hydrogen ingrowth, isotope exchange or contamination interactions occurring which degrade the standard; while some standards last beyond two years. Requirements could be set that would allow expired standard bottles that have held the integrity of the standard as expected.

6.0 References

1. A. ASTM A967 / A967M-17, "Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts," ASTM International, West Conshohocken, PA, 2017, www.astm.org; ASTM B912-02(2018), "Standard Specification for Passivation of Stainless Steels Using Electropolishing," ASTM International, West Conshohocken, PA, 2018, www.astm.org
2. Clark, E.A, et al., "Evaluation of Alternate Stainless Steel Surface Treatments for Mass Spectroscopy and Other Tritium Systems" SRNL-STI-2012-000181, 2012, Savannah River National Laboratory, Aiken, SC.
3. E.A. Clark, et al., "Evaluation of Alternate Stainless Steel Surface Treatments for Mass Spectroscopy and Other Tritium Systems" SRNL-STI-2012-000181, 2012, Savannah River National Laboratory, Aiken, SC.
4. Ajo, H.M., et al., "Analysis of Passivated Surfaces for Mass Spectrometer Inlet Systems by Auger Electron and X-ray Photoelectron Spectroscopy" SRNL-STI-2010-00394, 2010 Savannah River National Laboratory, Aiken, SC.
5. Peebles, H.; Moore, G.; Kotula, P.; Allen, A.; Jarek, R.; Bierner, J.; Fullmer, K.; "Characterization and Performance of the CTCV-2 Tritium Transportation and Storage Package" Tritium Focus Group Workshop, November 2015, Los Alamos, NM.
6. B. Bouarab, R., Bennici, S., Mirodatos, C., & Auroux, A. (2014). Hydrogen production from the water-gas shift reaction on iron oxide catalysts. *Journal of Catalysts*, 2014.
7. Sasaki, Y. Tito. "Reducing SS 304/316 Hydrogen Outgassing to 2×10^{-15} torr/cm²s," *Journal of Vacuum Science & Technology A* 25.4 (2007): 1309-1311.
8. Korinko, P., Wyrwas, R., Spencer, W., Peters, B., Stein, E. and Hitchcock, D., 2017. "Stainless Steel Passivation Using Electropolishing and Thermal Treatments", *Fusion Science and Technology*, 71(3), pp.403-409.
9. First, Phillip, private communication.
10. Korinko P.S., Wyrwas R.B., inventors; Savannah River Nuclear Solutions LLC, assignee. Development of a passivated stainless steel surface. United States patent application US 15/484,210. 2018 Oct 11.
11. Stein, E. A., Korinko, P.S.; "Characterizing Electropolished and Heat Treated Stainless Steels," SRNL-STI-20160-00698, 2016 Savannah River National Laboratory, Aiken, SC.