

PNNL-32829

Alternate Methods for Cleaning Zirconium Plate

April 2022

Rick W Shimskey
Kirsten A Adams
Tiffany C Kaspar
Lucas E Sweet
Matthew J Olszta
Jesse B Lang
Zachary F Huber

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <<https://www.ntis.gov/about>>
Online ordering: <http://www.ntis.gov>

Alternate Methods for Cleaning Zirconium Plate

April 2022

Rick W Shimskey
Kirsten A Adams
Tiffany C Kaspar
Lucas E Sweet
Matthew J Olszta
Jesse B Lang
Zachary F Huber

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99354

Abstract

The United States High Performance Research Reactor Conversion Program identified the need to transition from highly enriched uranium fuel to low enriched uranium fuel for high power research and civil reactors. One of the fuel configurations selected for these reactors was a uranium (U) foil alloyed with 10% molybdenum (Mo). The U-10Mo fuel foil was then covered with a zirconium (Zr) interlayer and pressed into an aluminum cladding. Idaho National Laboratory prescribed a need to remove surface oxidation on the Zr prior to bonding it with U-10Mo fuel foil. To determine the best method of oxidation removal, a variety of polishing methods, including hand polishing with a diamond paste or Scotch-Brite™ pads, mechanically wet-polishing with abrasive belts, and chemical etching with hydrofluoric/nitric acid mixtures, were investigated on pre-polished Zircaloy 702 sheets purchased directly from the manufacturer. No change in surface roughness was detected using any of these methods relative to the as-received material. In fact, scanning electron microscopy detected grit from hand polishing with Amplex Grade 30 waste soluble diamond paste and Scotch-Brite™ pads. Visible staining was found, and fluorine detected via X-ray photoelectron spectroscopy on the flash etching samples. These contaminants were not seen on the as-received material.

In addition to the need to remove the oxide layer on the Zr prior to co-rolling, there are concerns that the Neolube debonding agent on the co-rolling may contaminate the Zr surface after co-rolling. The experimental results found that zirconium in contact with Neolube coated steel plates was easily cleaned with ethanol wiping after heat treating and no carbide inclusions remained on the surface.

Overall, all cleaning methods tested did not significantly change the surface roughness of the plates or reduce the oxide layer present on the zirconium. Carbon was found on all the samples, before and after cleaning, except for the flash etch samples which detected fluorine instead. The insignificant changes seen in the cleaned plates relative to the as received plates question the need for cleaning prior to rolling. Further investigation in the requirements for cleaning at this step is recommended. Current methods for cleaning the surface after hot rolling with alcohol appear sufficient. After hot rolling, if Neolube does peel off the can and onto the zirconium coated foil surface, a dry abrasive or diamond paste polish is not recommended due to the chance of abrasive being embedded into the surface. However, the ability of an etchant to lift the lubricant off the zirconium surface indicates that a spot etch method could work to clean specific spots where Neolube is present if the need arises.

Summary

The United States High Performance Research Reactor Conversion Program exists to transition from highly enriched uranium fuel to low enriched uranium fuel for high power research and civil reactors. One of the fuel configurations selected for these reactors was a uranium (U) foil alloyed with 10% molybdenum (Mo). The U-10Mo fuel foil was then covered with a zirconium (Zr) interlayer and pressed into an aluminum cladding. The U-10Mo fuel foil was selected due to its high intrinsic U density and good mechanical properties. The Zr interlayer, which is bonded to the U-10Mo fuel foil through a series of hot co-rolling steps while the Zr and foil are sealed inside of a steel can, exists to prevent chemical interactions between the U-10Mo and Al. Idaho National Laboratory identified a need to remove surface oxidation on Zr to ensure a good bond to the U-10Mo fuel foil. A hand polishing method with a diamond grit buff compound currently is employed; however, better options may be available. The purpose of this report is to investigate surface finish and contaminants following several Zr cleaning methods.

The current process of hand polishing the surface utilizing the Amplex Grade 30 diamond paste was initially evaluated. The method was very dependent on the effort applied buffing off the compound with the edges being difficult to remove. A residue on the surface was detected by SEM with 1 μm grit particles embedded into the surface. Carbon, oxygen, silicon, and nitrogen were also present on the surface, and SEM detected an oxide layer was still present after cleaning, but no carbide inclusions were found.

Wet polishing trials at the 3M™ utilizing Trizact™ belts were performed as an alternate method for cleaning prior to rolling. Samples were analyzed via laser confocal microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and scanning electron microscopy (SEM). It was noted that the surface roughness was comparable to results seen using the same grade of belts tested with aluminum. Carbon, oxygen, and sulfur were found on the surface. However, no carbide or abrasive inclusions were found via SEM. This method, followed by ethanol and acetone cleaning, provides a surface that is as good or better than the diamond grit buffing.

Flash etching zirconium was also evaluated as an alternate cleaning method prior to rolling. Several etches in varying concentrations of nitric acid (HNO_3) and hydrofluoric acid (HF) were carried out for both 20 seconds and 40 seconds. The HNO_3 concentrations were 30% and 40%. The HF concentrations were 0.5%, 1.0%, 1.5%, and 2.0%. Each sample was analyzed visually and via laser confocal microscopy. No significant changes in surface roughness were found. Increases in HF concentration resulted increased variable mass loss (and dimensional change), but changes in HNO_3 and time had little impact on the variability of mass loss from this process. Although no carbon was detected on the surface using this technique, similar levels of oxide were present as with other techniques. Staining increased with higher HF concentrations, likely due to the increased heat generation from the faster kinetics of reaction at the surface. Also, laboratory constraints prevent the use of adequate water to quench the reaction rate upon removal from the etching solution, making it difficult to eliminate the staining witnessed here. This may not be a concern in a manufacturing setting. Overall, this method provides a trade-off with diamond grit buffing as having eliminated the carbon contamination but producing HF contamination instead.

The effectiveness of alcohol as a method of removing residual Neolube on the zirconium-uranium foils after hot rolling was also evaluated. To evaluate this approach, zirconium sheets were heat treated between two steel plates coated with Neolube. After the heat treatment, they were hand wiped with alcohol soaked Wypall® wipes. The zirconium sheets were analyzed via

laser confocal microscopy with SEM and optical spectrometry. There were no changes in surface roughness; however, carbon and oxygen were found on the surface. No inclusions were found via SEM. The current method of cleaning the co-rolled foils with alcohol appears to be adequate.

Cleaning tests were performed on zirconium sheets where Neolube was coated directly on their surface and the sheets were then heat treated under hot rolling conditions. Wypall® wipes soaked in ethanol were able to remove most of the graphite from the surface, but regions of carbon remained. Spectroscopy found carbon and oxygen present, but SEM did not find carbide inclusion on the surface. Afterwards, cleaning with Scotch-Brite™ pads and the Amplex diamond paste were utilized to remove the remainder on the surface. Carbon and oxygen were still found on the surface, but grit inclusions were also found via SEM from both methods. The final sample set was flash etched in HNO_3 and HF following the ethanol cleaning. The remaining lubricant was easily lifted from the surface but did not dissolve into the etchant solution. Spectroscopy found no carbon was present on the surface, but it was replaced by fluorine, most likely from the etchant. Staining occurred but the use of acid etch could be utilized as a “spot etch” method to clean places where Neolube is on the surface while minimizing the impact of the staining. No significant changes in surface roughness were measured from all cleaning trials and an oxide layer was still present.

Overall, all the cleaning methods leave behind some form of contamination without reduction in the oxide layer. Further understanding is needed as to why there is a requirement to cleaning the zirconium sheets prior to hot rolling. It is suggested that instead of in-house polishing, the Zr sheets used for fuel fabrication be cut and polished elsewhere prior to application to the U-10Mo fuel packet. Spot etching using HF and HNO_3 can be used to remove minor amounts of Neolube stuck to the plate after co-rolling, as necessary.

Acknowledgments

This work was funded by the U.S. Department of Energy and the National Nuclear Security Administration's Office of Material Management and Minimization and performed at Pacific Northwest National Laboratory under contract DE-AC05-76RL01830.

Acronyms and Abbreviations

Al	aluminum
C-DIC	C-laser differential interference contrast
EDS	energy-dispersive spectroscopy
F	fluorine
HF	hydrofluoric acid
HNO ₃	nitric acid
LCM	laser confocal microscopy
O	oxygen
S	sulfur
SEM	scanning electron microscopy
U	uranium
U-10Mo	uranium alloyed with 10% molybdenum
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Zr	zirconium

Contents

Abstract.....	ii
Summary	iii
Acknowledgments.....	v
Acronyms and Abbreviations.....	vi
1.0 Introduction	1
2.0 Materials and Methodology.....	2
2.1 Materials and Evaluation Methods of Cleanliness	2
2.1.1 Zirconium Cleaning Testing Materials.....	2
2.1.2 Evaluation Methods of Cleanliness	4
2.2 Cleaning Methods Evaluated for As-Received Material.....	5
2.2.1 Hand Polishing with Amplex Diamond Paste	5
2.2.2 Wet Polishing Testing at 3M	6
2.2.3 Flash Acid Etching.....	6
2.3 Cleaning Methods Evaluated for Post-Rolling	6
2.3.1 Alcohol Cleaning after Heat Treated Samples in Contact with Neolube.....	7
2.3.2 Removal of Neolube from Zirconium Foil.....	7
3.0 Results and Discussions	9
3.1 Hand Polishing with Diamond Paste Results.....	9
3.2 Wet Polishing Testing at 3M	12
3.3 Flash Etching Studies	16
3.3.1 Flash Etch Set 1: 30% HNO ₃ – Etch Time of 20 Second	16
3.3.2 Flash Etch Set 2 and 3: Varying Etch Time Between 20/40 Seconds	18
3.3.3 Flash Etch Sets 4 and 5: 40% HNO ₃ – Etch Times of 20 Second and 40 seconds	23
3.3.4 Acid Etching Discussion	27
3.4 Alcohol Cleaning of Heat-Treated Samples in Contact with Neolube-Coated Steel Plate	28
3.5 Cleaning Zirconium with Neolube Present	31
3.5.1 Ethanol Cleaning	31
3.5.2 Scotch-Brite™ Polishing	34
3.5.3 Flash Etching.....	39
3.6 Comparison of Zirconium Cleaning Test Results and Operational Considerations for Implementation.....	44
4.0 Conclusions.....	46
5.0 Quality Assurance	47
6.0 References.....	48

Figures

Figure 1.	The 50x and 20x magnification images of As-Received 702 Zirconium Sheet.....	2
Figure 2.	XRD Scan of As-Received 702 Zirconium Sheet.....	2
Figure 3.	SEM Surface Scan Images of As-Received 702 Zirconium Sheet at x2k and x10k Magnification	3
Figure 4.	Amplex Grade 30 Water Soluble Abrasive Diamond Paste	5
Figure 5.	Divisions of each sheet evaluated before and after cleaning.....	8
Figure 6.	Application of the diamond paste to zirconium sheet and results of hand polishing top third of sheet	9
Figure 7.	Comparison of the Ra, Rz, Sa, and Sz before and after polishing with diamond paste for each sheet.....	10
Figure 8.	The 10x magnification C-DIC images from Sheet 1 before and after polishing with the diamond grit buff compound.....	10
Figure 9.	XPS Scan of Zirconium Plate after Diamond Paste Polish	11
Figure 10.	SEM images for the samples polished by hand. Images a) and b) represent two regions analyzed at 10,000x magnification. The inclusions are remnants of the diamond grit paste.....	11
Figure 11.	SEM cross section images showing the oxide layers for the hand-polished sheets.....	12
Figure 12.	The Zr sheet following wet polishing at 3M.....	12
Figure 13.	The locations of LCM data collection for the wet-polished Zr sheets.....	13
Figure 14.	C-DIC images for rows 1 and 3 at 20x magnification.....	14
Figure 15.	XPS results for wet polished surface.....	14
Figure 16.	SEM images at three different locations on sample C2	15
Figure 17.	Flash etching Set 1 samples compared to a color chart. Each etched sample had brown staining and more of a matte finish than the shinier, silver baseline sample.....	16
Figure 18.	Comparison of the Ra, Rz, Sa, and Sz values before and after etching for Set 1 samples etched in 30% HNO_3 and varying concentrations of HF.....	17
Figure 19.	C-DIC images at 20x magnification for Set 1 etched samples in 30% HNO_3 and varying concentrations of HF.....	17
Figure 20.	Etch Set 2 samples compared to a color chart from the duplicate flash etch testing at 30 wt% nitric and varying hydrofluoric concentrations. Etch time was 20 seconds.....	18
Figure 21.	Comparison of the Ra, Rz, Sa, and Sz values before and after etching for Etch Set 2 samples etched for the duplicate in 30% HNO_3 and varying concentrations of HF. Each etch lasted for 20 seconds.....	19
Figure 22.	C-DIC images at 20x magnification from etched Set 2 samples from the duplicate testing at 30% HNO_3 and varying concentrations of HF. Each etch lasted for 20 seconds	19

Figure 23.	Set 3 samples etched at 30 wt% nitric and varying hydrofluoric concentrations compared to a color chart. Etch time was for 40 seconds.....	20
Figure 24.	Comparison of the Ra, Rz, Sa, and Sz values before and after etching for Set 3 samples etched in 30% HNO_3 and varying concentrations of HF. Each etch lasted for 40 seconds.	21
Figure 25.	C-DIC images at 20x magnification for Set 3 samples etched in 30% HNO_3 and varying concentrations of HF. Each etch lasted for 40 seconds.	21
Figure 26.	Comparison of the Set 4 post-etch samples and a color chart etched in 40wt% HNO_3 at varying HF concentrations. The etch time was 20 seconds.	23
Figure 27.	Comparison of the Ra, Rz, Sa, and Sz values before and after etching Set 4 samples etched in 40wt% HNO_3 and varying concentrations of HF. Each etch lasted 20 seconds.	24
Figure 28.	C-DIC images at 20x magnification for Set 4 samples etched in 40% HNO_3 and varying concentrations of HF. Each etch lasted for 20 seconds.	24
Figure 29.	Comparison of the Set 5 post-etch samples and a color chart etched in 40wt% HNO_3 at varying HF concentrations. Etch time was 40 seconds.	25
Figure 30.	Comparison of the Ra, Rz, Sa, and Sz values before and after the Set 5 were etched in 40wt % HNO_3 and varying concentrations of HF. Each etch lasted for 40 seconds.	26
Figure 31.	C-DIC images at 20x magnification for the Set 5 samples etched in 40% HNO_3 and varying concentrations of HF. Each etch lasted for 40 seconds.	26
Figure 32.	Sheets 1–3 before and after heat treatment between two Neolube-coated, stainless-steel sheets.....	28
Figure 33.	Ra, Rz, Sa, and Sz values for Sheet 2 before and after alcohol cleaning after heat treatment in contact with Neolube.	29
Figure 34.	C-DIC images at (a) 50x and (b) 20x magnification of Sheet 2 before and after alcohol cleaning after heat treatment in contact with Neolube.....	29
Figure 35.	SEM surface images from Plate 2 after alcohol cleaning after heat treatment in contact with Neolube	30
Figure 36.	Ra, Rz, Sa, and Sz values for Section A cleaned with ethanol before and after heat treatment and Neolube removal. There was little difference in surface roughness values.	31
Figure 37.	The 10x magnification C-DIC images before and after heat treatment and Neolube removal with ethanol.	32
Figure 38.	XRD scan of alcohol clean plate heat treated with Neolube on surface. Similar pattern found on as-received material.	33
Figure 39.	SEM images for the samples cleaned with ethanol. Images a), b), and c) represent three different regions analyzed at 10,000x magnification. These images show no carbide inclusions.	33
Figure 40.	Oxide layers found on the ethanol cleaned sheets.....	34
Figure 41.	Scotch-Brite Pads (a) used for cleaning. Strip C1 before (b), during (c), and after cleaning (d).	35

Figure 42.	Comparison of the Ra, Rz, Sa, and Sz values before and after polishing with Scotch-Brite™ to remove residual Neolube on surface of heat-treated zirconium.	36
Figure 43.	The 10x magnification C-DIC images for Section C from Sheet 1 before and after polishing with the Green Fine Grade Scotch-Brite pads to remove residual Neolube on surface of heat-treated zirconium.	36
Figure 44.	The 10x magnification C-DIC images from Section C of Sheet 3 before and after hand polishing with the Ultra Fine Scotch-Brite™ pad to remove residual Neolube on surface of heat-treated zirconium.	37
Figure 45.	XPS scans of hand polished surface using Scotch-Brite™ pad to remove residual Neolube on surface of heat-treated zirconium.	37
Figure 46.	SEM images for samples polished using Scotch-Brite™ pads. Images a) and b) represent locations analyzed at 10,000x magnification.	38
Figure 47.	SEM images for the Scotch-Brite™ polished sheets. An oxide layer is visible on each sheet.	38
Figure 48.	The flash etching process for removing residual Neolube from heat-treated zirconium.	40
Figure 49.	Comparisons of the Ra, Rz, Sa, and Sz values before and after flash etching with HF/nitric acid mixture to remove residual Neolube on surface of heat-treated zirconium.	41
Figure 50.	The 10x magnification C-DIC images before and after flash etching with HF/nitric acid mixture to remove residual Neolube on surface off heat-treated zirconium.	41
Figure 51.	XPS scans of flash etched heat-treated zirconium using HF/nitric acid mixture to remove residual Neolube from surface.	42
Figure 52.	SEM images for etched samples. Images a), b), and c) represent the three locations imaged at 10,000x magnification. No inclusions were found on the surface.	42
Figure 53.	The SEM images for the cross sections of the flash etched sample with indication of oxide layer present.	43

Tables

Table 1.	Ra, Rz, Sa, and Sz values for wet-polished 3M sheet. The average Ra is 0.578 (± 0.122) μm . The average Rz is 5.092 (± 0.784) μm . The average Sa is 0.609 (± 0.138) μm . The average Sz is 11.088 (± 1.436) μm	13
Table 2.	The mass changes for the 20 second and 40 second etches in 30% HNO_3 with varying concentrations of HF.	22
Table 3.	The mass change for each sample etched in 40% HNO_3 and varying concentrations of HF.....	27
Table 4.	Summary of Zirconium Cleaning Test Results	45

1.0 Introduction

The United States High Performance Research Reactor Conversion Program exists to transition from highly enriched uranium fuel to lowly enriched uranium fuel for high power research and civil reactors. One of the fuel configurations selected for these reactors was a uranium (U) foil alloyed with 10% molybdenum (Mo). The U-10Mo fuel foil was then covered with a zirconium (Zr) interlayer and pressed into an aluminum cladding. The U-10Mo fuel foil was selected due to its high intrinsic U density and good mechanical properties. The Zr interlayer, which is bonded to the U-10Mo fuel foil through a series of hot co-rolling steps while the Zr and foil are sealed inside of a steel can, exists to prevent chemical interactions between the U-10Mo and Al.

The U-10Mo fuel ingot is first prepared through melting, casting, and homogenization. Once homogenized, the Zr interlayer is attached through a series of hot-rolling and annealing steps before finally being cold rolled to final thickness. The hot rolling process is performed by canning the ingot with Zr sheets on either side. Cold rolling, in contrast, is done in open air and does not require canning. The fuel plate product is prepared by hot isostatic pressing, which bonds the Al 6061 cladding to the fuel foil to fabricate the fuel plate.

Prior to canning, the Zr sheet is sheared to size, cleaned, and polished. Idaho National Laboratory identified a need to remove surface oxidation on Zr to ensure a good bond to the U-10Mo fuel foil. Amplex Grade 30 water soluble diamond abrasive paste is applied using a lint-free cloth. Polishing is continued for approximately 3 minutes, or until the surface is shiny. The polish residue is removed using ethanol, and the Zr sheets then are placed in the steel rolling cans with the fuel billet.

The current polishing method requires significant effort and is believed not to be entirely adequate for removing surface oxidation. As a result, several polishing methods were identified and investigated for this report to provide a comparison to the standard process. These alternate methods include wet-polishing, etching with nitric acid (HNO_3) and hydrofluoric acid (HF), ethanol cleaning, and polishing Scotch-Brite™ pads.

After de-canning, the Zr/U-10Mo foil is cleaned with alcohol. There is the possibility that the Neolube® used to prevent the Zr from bonding to the steel can may contaminate the surface of the foil. A study was performed to evaluate this and other cleaning methods adequately cleaning the surface after the hot rolling process.

To evaluate the efficacy of these cleaning process, data on surface roughness was obtained using laser confocal microscopy (LCM) and information on contaminants and inclusions measured using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM).

2.0 Materials and Methodology

2.1 Materials and Evaluation Methods of Cleanliness

2.1.1 Zirconium Cleaning Testing Materials

Sheets of 702 Zirconium (Zr) were acquired to test different cleaning methods utilized before and after hot rolling of zirconium to uranium. The plates were nominally 12 inches by 24 inches in size with thickness either 0.020 inch or 0.040 inch and received with an initial polish with measured surface roughness ranging between 0.2-1.0 μm (8-40 μin) Ra, measured by LCM. The 50x and 20x magnification C-DIC images are shown in Figure 1. XRD and surface analysis with SEM was also performed on the as-received material. XRD found carbon compounds on the surface that were identified as carbides (Figure 2). However, surface scans by SEM (Figure 3) did not find carbide inclusions on the surface so the carbon recognized by XRD is likely part of the microstructure of the purchased material and not a surface defect.

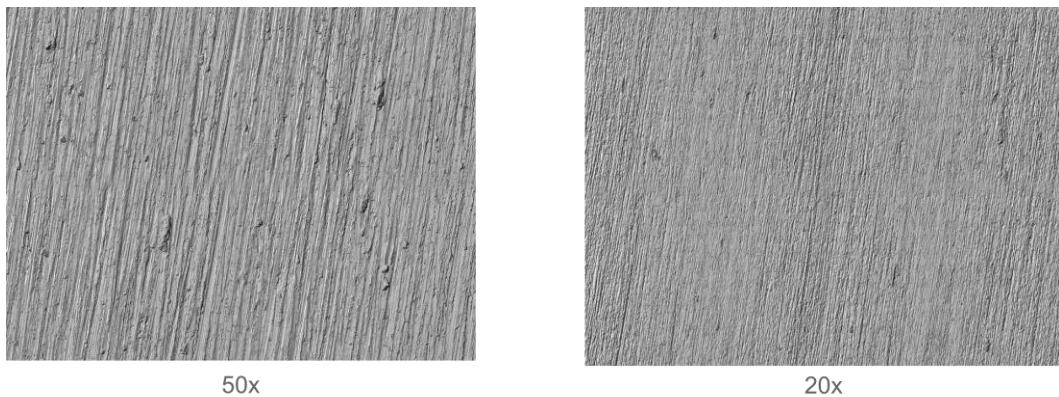


Figure 1. The 50x and 20x magnification images of As-Received 702 Zirconium Sheet.

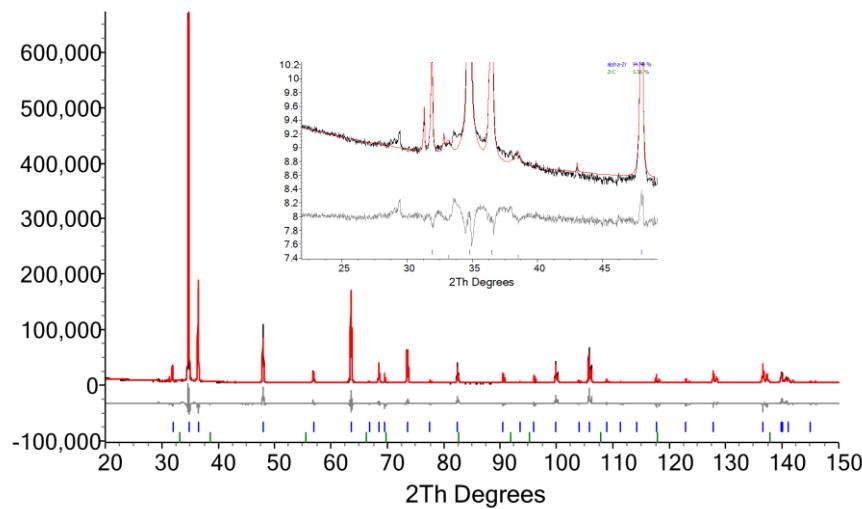


Figure 2. XRD Scan of As-Received 702 Zirconium Sheet.

Note: The blue markers identify peaks associated with Zr metal while the green markers identify peaks associated with zirconium carbide.

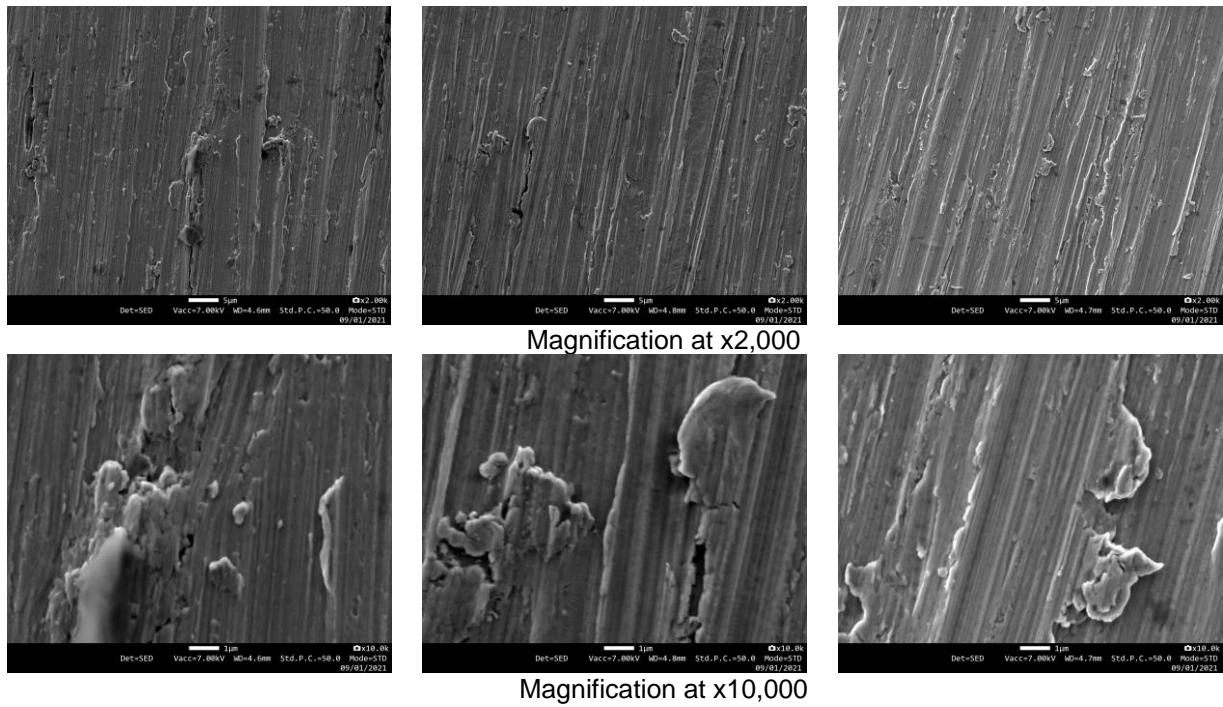


Figure 3. SEM Surface Scan Images of As-Received 702 Zirconium Sheet at x2k and x10k Magnification

Materials for cleaning used for this testing:

- Amplex Grade 30 Water Soluble Diamond Paste (Figure 4)
- 3M Wet-polishing Triazat™ abrasive belts (253FA; Grades A80/A45/A30)
- Scotch-Brite™ polishing pads (Grades Fine and Ultra Fine)
- Neolube No.1 Dry Film Graphite Lubricant
- Laboratory grade chemicals
 - Ethanol
 - Hydrofluoric Acid
 - Nitric Acid
- Deionized water

2.1.2 Evaluation Methods of Cleanliness

There are four areas that are focused on to evaluate the effectiveness of the cleanliness.

- **Visual Appearance**

- *Description:* While visual appearance is frequently called a cosmetic attribute to cleanliness, the statement “*If it doesn’t look clean, it isn’t clean*” is to evaluate a cleaning/finishing process. Surfaces of cleaned material are expected to be free of smut, manufacturing debris, oil and grease, and uniform in appearance. Visual standards are commonly used for this when other quantification methods are not available. When the cleaned surface does not appear uniform, it can be an indicator of other issues such as irregular oxide growth, surface contamination, or an issue with the finishing operation are present (e.g., abrasive belt wearing out, insufficient rinse).
- *Quantification Method:* The visual appearance before and after cleaning is discussed, documenting this with digital pictures.

- **Surface Roughness**

- *Description:* Surface roughness is the measurement of the surface texture of a material that examines the total spaced irregularities on the surface by measuring the height difference of these irregularities using either a surface profilometer with a contact stylus or using an optical surface method like a laser confocal microscope. This technique is useful to quantify if a surface is considered “rough” or “smooth” of a material. It is also used to measure effectiveness of a finishing process and variability.
- *Quantification Method:* Surface roughness is performed using a Keyence VT laser confocal microscope which measures the surface roughness while imaging the surface. Measurement of samples are performed before and after cleaning to evaluate the change in surface roughness and provide a close-up visual of the surface for comparison. Ra and Rz (average and maximum differences found across a linear span) were measured before and after cleaning/finishing steps, as well as Sa and Sz (average and maximum differences found across an area region).

- **Oxide Removal**

- *Description:* Oxide removal is a frequent goal of finishing operations, but difficult to quantify without optical methods unless the oxide is a visible layer. In many cases, assumptions are made on the effectiveness of the removal of an oxide layer without realizing that oxide layer growth occurs with refractory metals, like zirconium, naturally with the presence oxygen in air and water quickly after its removal.
- *Quantification Method:* X-Ray photoelectron spectroscopy (XPS) is used to examine the surface of metal surfaces before and after cleaning for the presence of oxygen on the surface and indications of oxygen-zirconium bonds confirming the presence of an oxide layer. Scanning electron microscopy (SEM) is

performed on polished cross-sections of the cleaned surface to examine the oxide layer surface and quantify its thickness. X-ray diffraction (XRD) was also performed but was not sensitive enough to identify the thin layers of oxide present on the samples before and after cleaning.

- **Surface Contamination**

- *Description:* Depending on how the material is used after cleaning/finishing, surface contamination either left behind or not removed from an operation is a concern. Oil and grease contamination can cause operational problems with the vacuum system on an annealing furnace as well as producing unwanted reactions with the metal at higher temperatures to produce carbide inclusions. Other elemental contaminations that impact corrosion or issues to operations downstream are also a concern and typically controlled by the components of the cleaning/finishing material utilized. However, most cleaning methods leave something behind but not necessarily visible. Optical spectroscopy techniques can assist in identify unwanted particulate, inclusions, and elemental bonds on the surface that cannot otherwise be seen.
- *Quantification Method:* XPS and XRD are both used to examine elemental contamination found on the surface. SEM with energy-dispersive spectroscopy (EDS) was also used to scan the surface for the presence of carbide inclusion or other finishing materials, such as abrasive particles.

2.2 Cleaning Methods Evaluated for As-Received Material

At BWXT the as-received Zr foils are currently polished prior to their use in co-rolling. This is done using a diamond paste. This study compared the surface finish of the as-received material and baseline diamond polishing technical to wet polishing and flash acid etching. The experimental techniques used for each method are described below.

2.2.1 Hand Polishing with Amplex Diamond Paste

The baseline process for cleaning the as-received zirconium uses Amplex Grade 30 water soluble diamond abrasive paste (Figure 4). This approach was evaluated using a 2-inch by 6-inch strip of zirconium plate. The paste was applied to the surface of the plate and then hand-polished until all the compound was removed from the surface. Measurements of the surface roughness were evaluated at three 1.25-inch square locations on the sample before and after cleaning. These locations were subsampled afterwards and evaluated for oxide thickness by SEM and contamination by spectrometry.



Figure 4. Amplex Grade 30 Water Soluble Abrasive Diamond Paste

2.2.2 Wet Polishing Testing at 3M

Four plates (0.040 inch thickness) were sent to the 3M testing facility to examine wet polishing as a preparation method for Zr prior to hot rolling. A two-head Timesaver Lynx wet polisher was utilized with the following conditions for all four plates:

- Belt speed of 3500 sfpm
- Contact roll of 45A durometer
- Load setting of 25% of maximum
- Conveyor speed of 5 fpm
- Three polishing belt process using wet Trizact™ belts (253FA; Grades A80/A45/A30), using only one belt at a time
- Water based emulsion used for coolant during testing

For these tests, only one side of the plate was polished, with an average dimensional removal of about 0.6 mils (0.0006 inch) from the wall per pass. One of the plates was evaluated afterwards. The plate was divided into three, 2-inch strips with three, 1.25 x 1.25-inch squares per strip. Each location was analyzed via LCM at 50x and 20x magnifications and by optical spectroscopy for contaminants.

2.2.3 Flash Acid Etching

Chemical flash etching of zirconium was performed to investigate cleaning of zirconium prior to hot rolling. Square coupon samples (nominally 1.5 inches) were cut from 0.020-inch-thick plate to perform testing with hydrofluoric/nitric acid solutions. Concentrations of hydrofluoric acid were allowed to vary between 0.5 wt% to 2.0 wt% while concentrations of nitric acid were tested at 30 wt% and 40 wt%. Etch times of 20 and 40 seconds were also tested to understand the impact on the surface.

The following procedure was used for etching:

1. Soak in deionized water for 20 seconds
2. Etch in acid solution for 20/40 seconds
3. Rinse
4. Soak in deionized water for 5 minutes
5. Rinse
6. Soak in hot sink water for 45 minutes.

All squares and a baseline sample were analyzed on each side via LCM at 50x and 20x magnifications and evaluated for contaminants by spectroscopy.

2.3 Cleaning Methods Evaluated for Post-Rolling

During hot co-rolling, BWXT uses Neolube to prevent the steel rolling can from bonding to the Zr. An alcohol wipe is used to clean the Zr surface in preparation for subsequent steps. The experimental techniques used to evaluation of the current method of Neolube removal are described below.

2.3.1 Alcohol Cleaning after Heat Treated Samples in Contact with Neolube

To simulate surface conditions after hot rolling, three zirconium plates (0.020 inch thickness) were heat treated in contact with two steel sheets coated with Neolube. The steel plates were initial coated with the graphite lubricant and left to dry overnight. Once dry, they were heated to 350°C and held for an hour to cure the lubricant to the steel plates.

Once the steel plates were cooled, the three zirconium plates were place between the two steel plates and placed inside a vacuum furnace so both sides were in contact with the dry lubricant. The plates were then heat treated to 675°C for an hour to simulate temperatures zirconium reaches during hot rolling. Upon cooling, the zirconium plates were taken out of the vacuum furnace and removed from the Neolube coated steel plates. The zirconium plates were then cleaned using the baseline approach which was a wipe-down with ethanol.

The sheets were initially analyzed by LCM prior to this heat treatment and re-analyzed afterwards to see if any changes in the surface were visible seen. The plate surfaces were also analyzed by SEM and spectroscopy to look for carbide inclusions on the surface and for residual contamination.

2.3.2 Removal of Neolube from Zirconium Foil

To evaluate cleaning methods after heat treatment if the Neolube lubricant were to become adhered to the rolled zirconium foil upon removal of the can, the Neolube lubricant was applied to a three 6-inch by 12-inch sheets of zirconium (0.020 inch thickness). These strips were cleaned with ethanol, and each sheet was numbered. The Neolube was allowed to dry overnight before the sheets were annealed in a vacuum furnace using the following program:

1. Hold at 5°C for 10 seconds to establish an initial baseline temperature
2. Ramp to 350°C for 60 minutes
3. Hold at 350°C for 60 minutes
4. Ramp at 675°C for 65 minutes
5. Hold at 675°C for 60 minutes
6. Cool overnight.

The plates were removed from the furnace and cleaned with ethanol and Wypall® wipes until no more Neolube was removed. Each sheet was divided into four 2-inch strips and three, 1.25 x 1.25-inch squares were marked in each strip for further analysis.

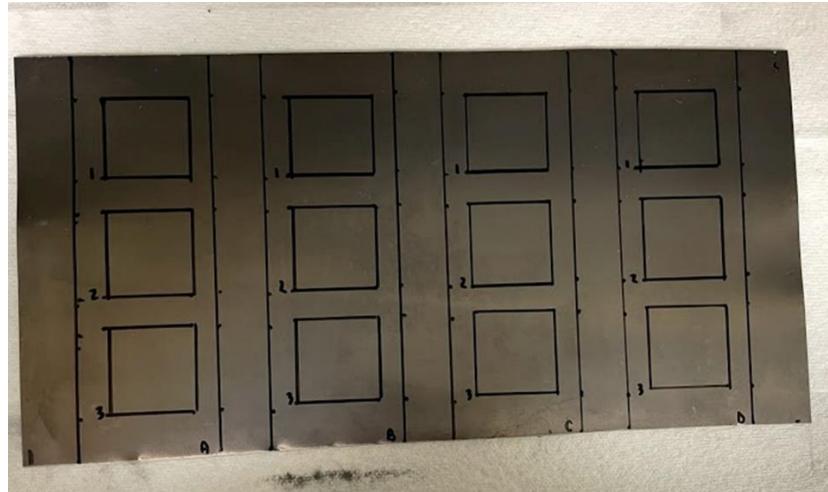


Figure 5. Divisions of each sheet evaluated before and after cleaning.

Each section was further processed in the following ways until Neolube was no longer visibly being removed from the surface:

- Polished with Scotch-Brite™ pads.
- Flash etched using 3 wt% HF and 30 wt% HNO₃.

After cleaning, the surface was re-evaluated with LCM to document changes in surface roughness. SEM was used to evaluate changes in the oxide layer and for the presence of carbide inclusions or other contaminants. Spectroscopy was also performed to examine elemental contamination present on the surface as well.

3.0 Results and Discussions

3.1 Hand Polishing with Diamond Paste Results

The diamond paste was applied to each section of a sheet as shown in Figure 6 and then hand polished over the surface of the metal. While the center of the sheet could be polished within a few minutes, a great deal of time was spent hand polishing the edges of the sheet to remove the polish. Figure 6 shows the initial results of polishing the top third of a sheet where the edges still show indications of the paste after 5 minutes, indicating that this process requires a great deal of effort and experience to perform well.

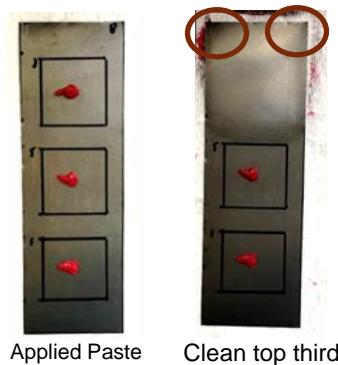


Figure 6. Application of the diamond paste to zirconium sheet and results of hand polishing top third of sheet

After cleaning, the markings were reapplied and each location was analyzed via LCM, XRD, XPS, and SEM. LCM was used to determine the surface roughness following polishing. XRD and XPS were utilized to determine if any surface contaminants were present on the surface. SEM was utilized to determine if any inclusions were present on the surface. A small square was cut from each sheet, potted, and polished in resin on its side, and the cross section was analyzed via SEM to determine if an oxide later remained on the surface.

An LCM data comparison is shown in Figure 7. The 10x magnification C-DIC images are shown in Figure 8. The LCM data indicates that the surface roughness was not improved by polishing with the red diamond grit paste as compared to the as-received sample.

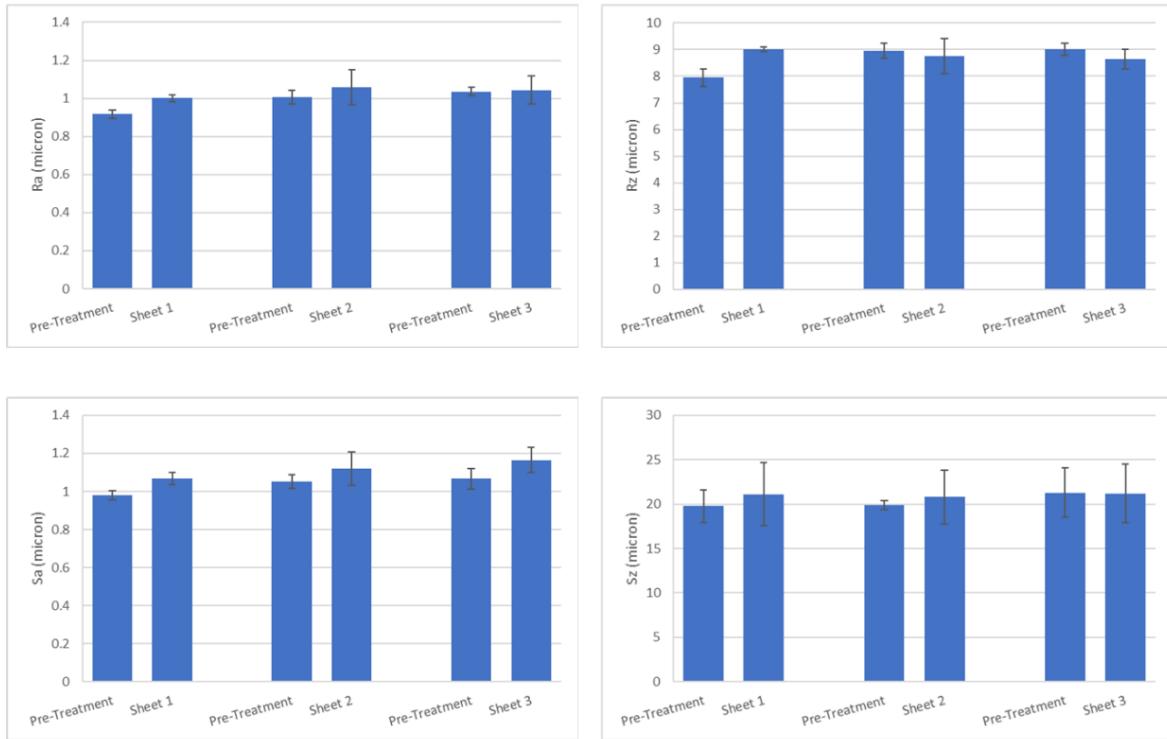


Figure 7. Comparison of the Ra, Rz, Sa, and Sz before and after polishing with diamond paste for each sheet.

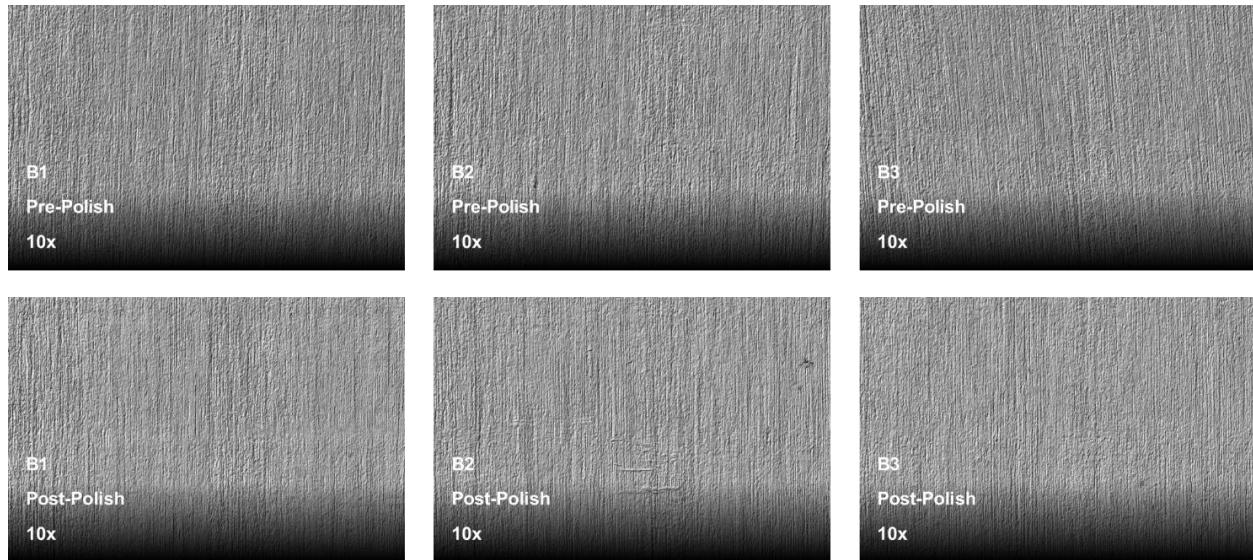


Figure 8. The 10x magnification C-DIC images from Sheet 1 before and after polishing with the diamond grit buff compound.

The XPS data (Figure 9) indicated the presence of oxygen and zirconium at a valence state (Zr^{+4}) indicating an oxide layer is still present even after polishing. Silicon and nitrogen were also detected which are present in the diamond grit paste. XRD indicated the presence of carbon at levels similar to the as-received sheet.

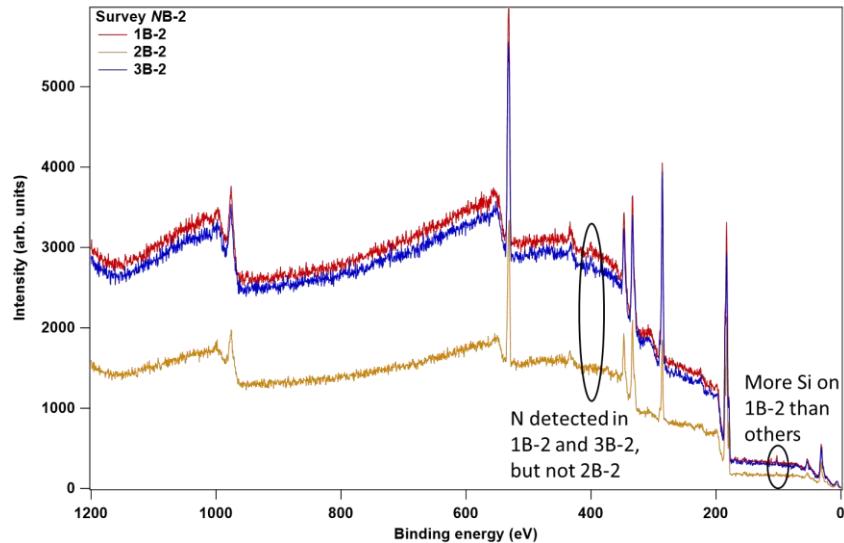


Figure 9. XPS Scan of Zirconium Plate after Diamond Paste Polish

Figure 10 shows SEM images of the polished surface with remnants of the diamond grit buff compound on or embedded zirconium surface, which correlates with the results from the XPS. Figure 11 shows the results of cross-sectional images of the polished sheet. As indicated from XPS, oxide layers were found present on the surface, with a measured thickness between 3 to 6 μm . While XRD indicated the presence of carbon, no carbide inclusions were seen on the surface by SEM.

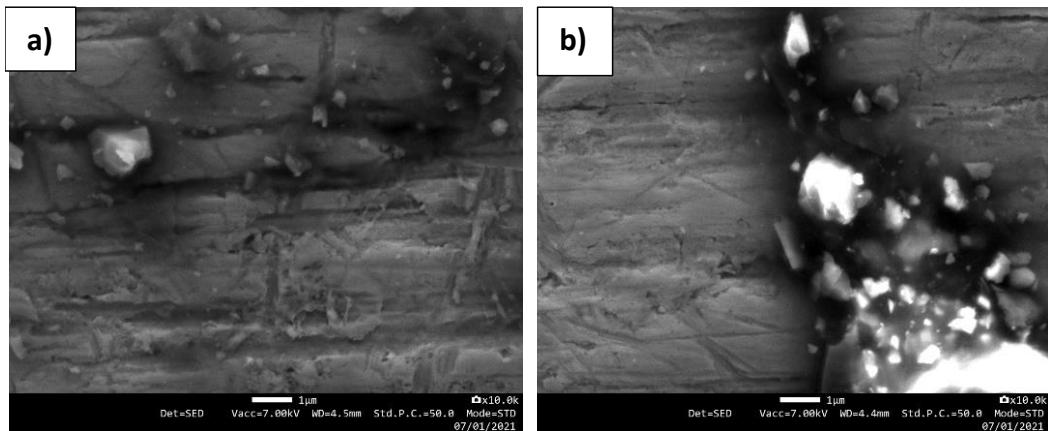


Figure 10. SEM images for the samples polished by hand. Images a) and b) represent two regions analyzed at 10,000x magnification. The inclusions are remnants of the diamond grit paste.

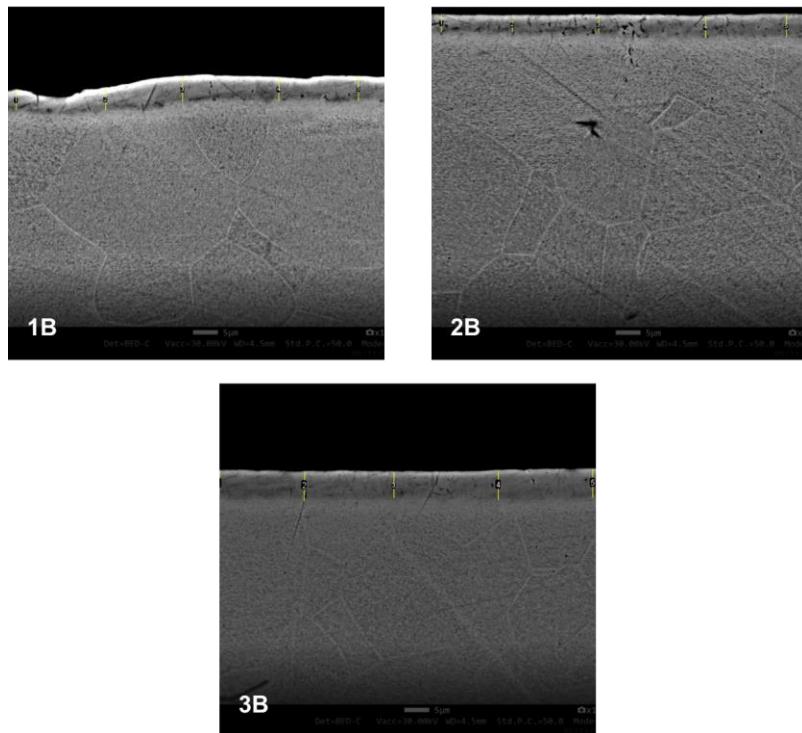


Figure 11. SEM cross section images showing the oxide layers for the hand-polished sheets.

3.2 Wet Polishing Testing at 3M

The Zr sheet following wet polishing at 3M is shown in Figure 12. Staining was found present on the surface from the water-soluble coolant not being completely cleaned off the surface upon exiting the wet polisher. Zirconium can easily stain after machining and either requires hand cleaning with a solvent (acetone/alcohol) that quickly dries or allowed to passivation in water to allow the oxide layer to grow to a level where irregular growth does not occur. While the impact is cosmetic, it indicates possible contaminates from the coolant may be present.



Figure 12. The Zr sheet following wet polishing at 3M.

LCM data was collected at nine separate locations shown in Figure 13 and the results are summarized in Table 1. These results indicate that the surface roughness of the wet polished

plate is slightly better than the as-received ($R_a = 0.9\text{-}1.0 \mu\text{m}$) and diamond polished plate ($R_a \sim 1.0 \mu\text{m}$). The C-laser differential interference contrast (C-DIC) images for each location are shown in Figure 14 for the 20x magnification and are within a surface roughness range expected from the Trizact™ belt sequence used for this testing.

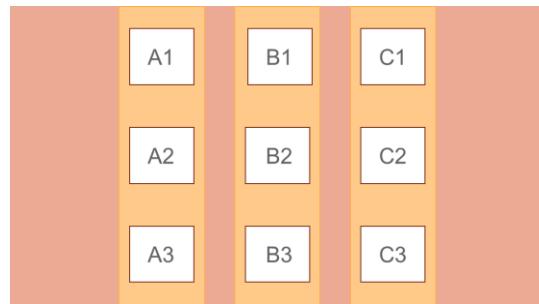


Figure 13. The locations of LCM data collection for the wet-polished Zr sheets.

Table 1. R_a , R_z , S_a , and S_z values for wet-polished 3M sheet. The average R_a is $0.578 (\pm 0.122) \mu\text{m}$. The average R_z is $5.092 (\pm 0.784) \mu\text{m}$. The average S_a is $0.609 (\pm 0.138) \mu\text{m}$. The average S_z is $11.088 (\pm 1.436) \mu\text{m}$.

	Average R_a (μm)	Std Dev R_a (μm)	Average R_z (μm)	Std Dev R_z (μm)	S_a (μm)	S_z (μm)
A1	0.682	0.142	5.938	1.040	0.724	11.196
A2	0.575	0.112	4.886	0.774	0.627	10.301
A3	0.496	0.153	4.801	1.847	0.495	10.536
B1	0.602	0.097	5.300	1.184	0.655	10.745
B2	0.660	0.176	4.542	0.763	0.712	12.440
B3	0.437	0.098	4.184	1.038	0.438	10.298
C1	0.761	0.108	6.041	1.346	0.814	12.988
C2	0.611	0.204	6.071	2.595	0.608	12.766
C3	0.379	0.047	4.068	1.315	0.407	8.524

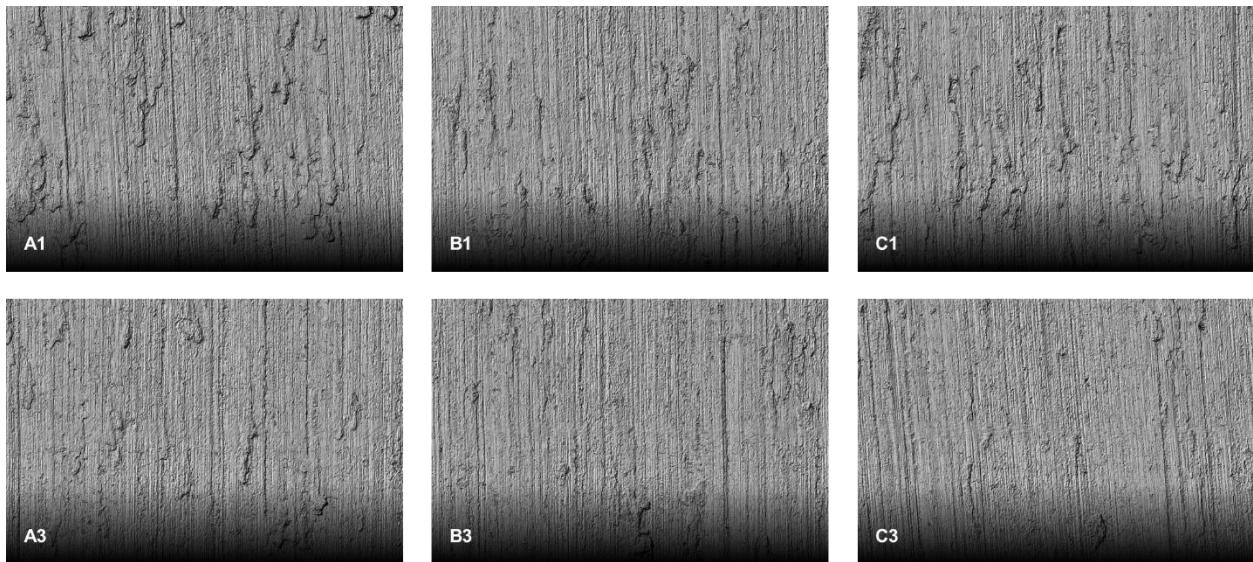


Figure 14. C-DIC images for rows 1 and 3 at 20x magnification.

XPS analysis indicated the presence of Zr, O, and trace amounts of sulfur as shown in Figure 15. The carbon and sulfur present were likely from the water-soluble coolant used for the polishing, and the zirconium again was seen at a valence state indicating the presence of an oxide layer, like the as-received sample. XRD analysis also found similar levels of carbon present as found in the as-received material.

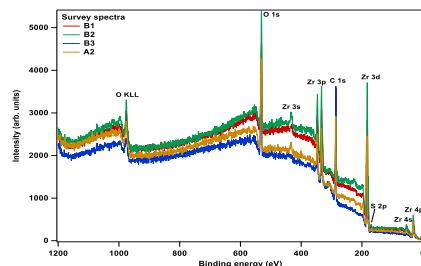


Figure 15. XPS results for wet polished surface

SEM images are shown in Figure 16, showing no abrasive or carbide inclusion were detected on the surface.

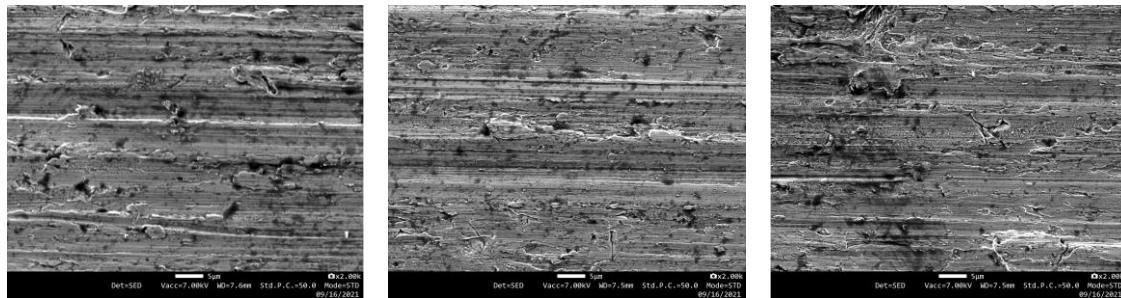


Figure 16. SEM images at three different locations on sample C2

3.3 Flash Etching Studies

Flash etching of nominal 1-inch square coupon were performed at varying acid concentrations and time periods (20 seconds and 40 seconds) to evaluate impacts on surface roughness and staining. Spectroscopy of the surface after flash etch was performed in a separate study (Section 3.5.3).

3.3.1 Flash Etch Set 1: 30% HNO₃ – Etch Time of 20 Second

Samples were etched for 20 seconds in etchant solutions with 30 wt% nitric acid and varying concentration of hydrofluoric acid (0.5 wt% to 2.0 wt%). The pre-etched baseline and etched samples visual appearances are compared to a color chart in Figure 17. Each etch had brown staining on the surface and an increase in surface roughness. As the concentration of HF was increased, the etch was faster, correlating to an increase in staining. LCM surface roughness measurements of baseline and etched sample were taken and summarized in Figure 18. The plates were consistently rougher after etching with nitric acid/HF as compared to the baseline diamond polished material. The 20x magnification C-DIC images are shown and Figure 19.

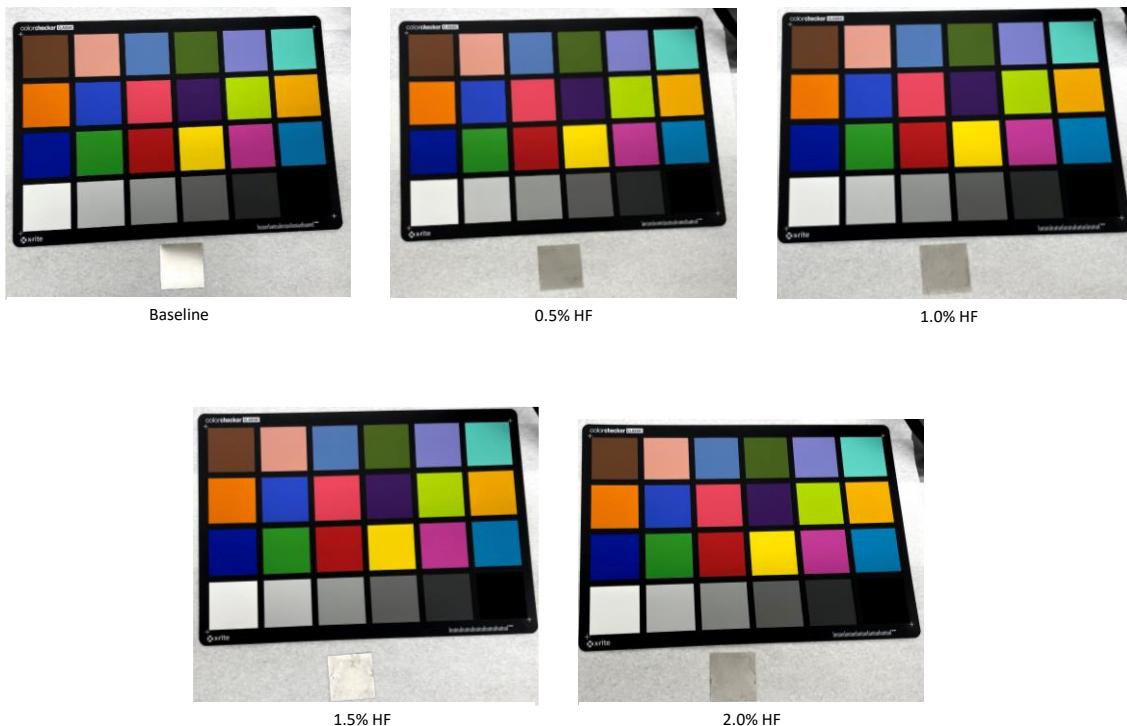


Figure 17. Flash etching Set 1 samples compared to a color chart. Each etched sample had brown staining and more of a matte finish than the shinier, silver baseline sample.

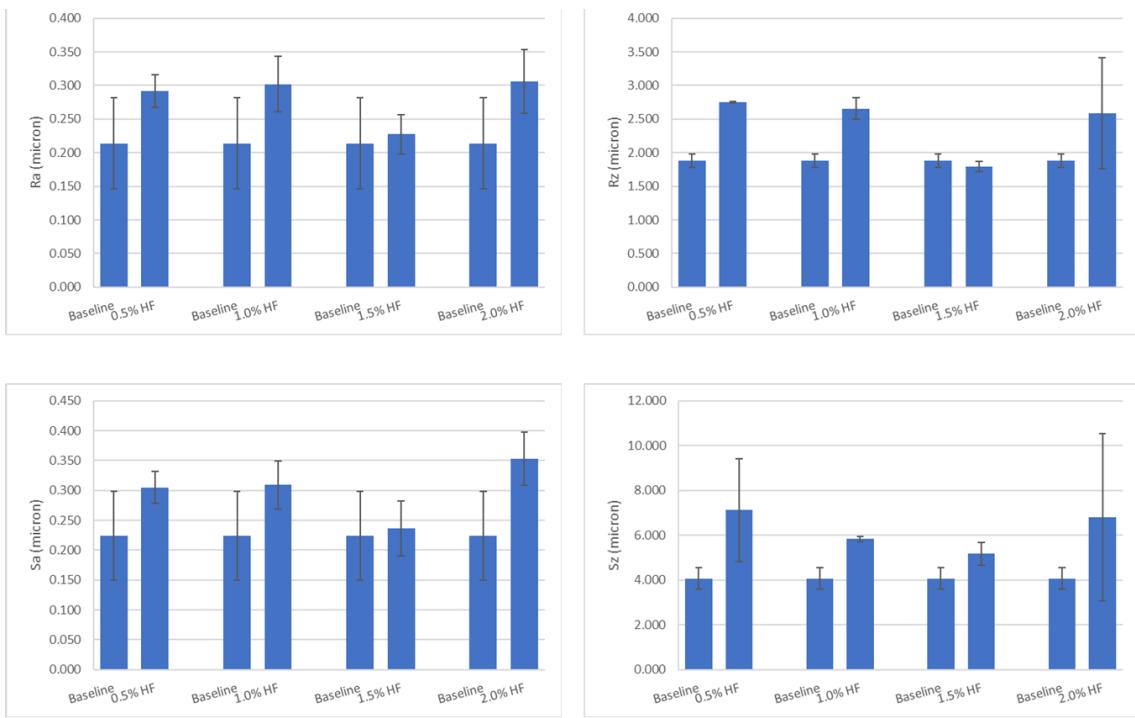


Figure 18. Comparison of the Ra, Rz, Sa, and Sz values before and after etching for Set 1 samples etched in 30% HNO₃ and varying concentrations of HF.

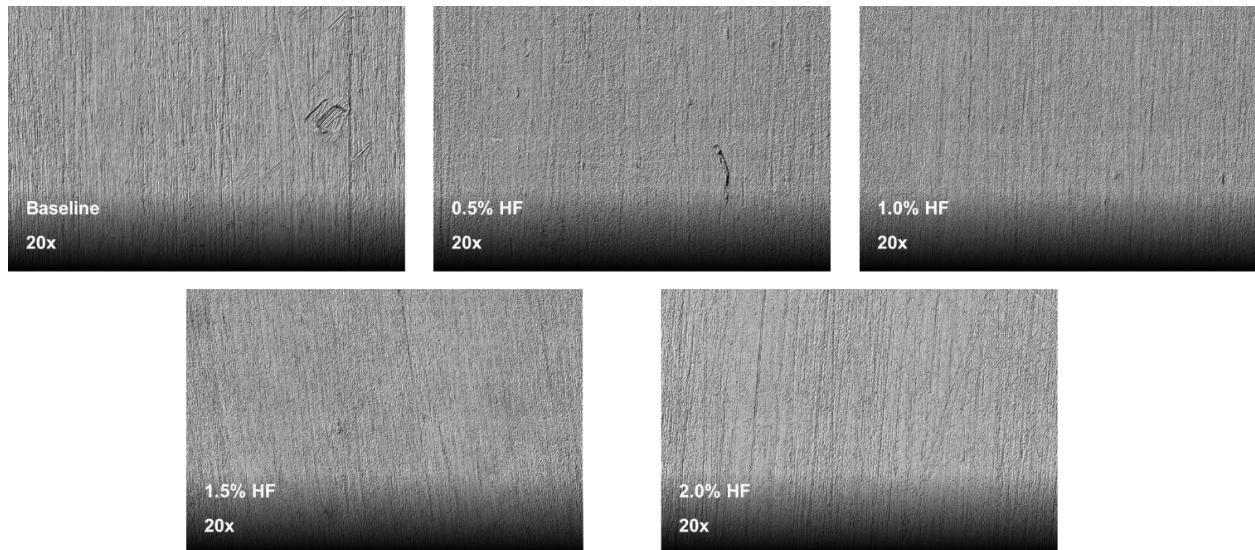


Figure 19. C-DIC images at 20x magnification for Set 1 etched samples in 30% HNO₃ and varying concentrations of HF.

3.3.2 Flash Etch Set 2 and 3: Varying Etch Time Between 20/40 Seconds

The initial set of flash etching testing (Set 1) at 30 wt% nitric acid and varying hydrofluoric acid conditions for 20 seconds was repeated (Set 2) to collect mass loss data. Images of each sample etched for 20 seconds is shown in Figure 20. The comparison data for each square and the baseline sample analyzed via LCM is shown in Figure 21. The 20x magnification C-DIC images are shown in Figure 22. Results were comparable to the first etch test with increases in surface roughness measured afterwards and increased staining with increasing hydrofluoric acid concentration.

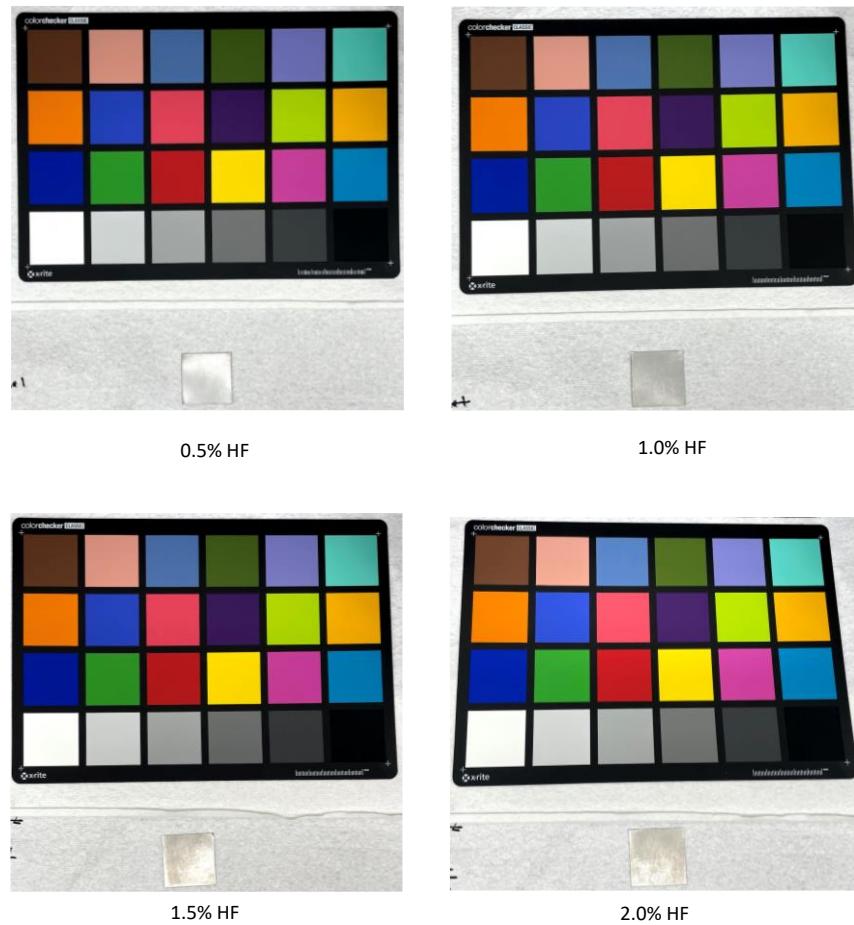


Figure 20. Etch Set 2 samples compared to a color chart from the duplicate flash etch testing at 30 wt% nitric and varying hydrofluoric concentrations. Etch time was 20 seconds.

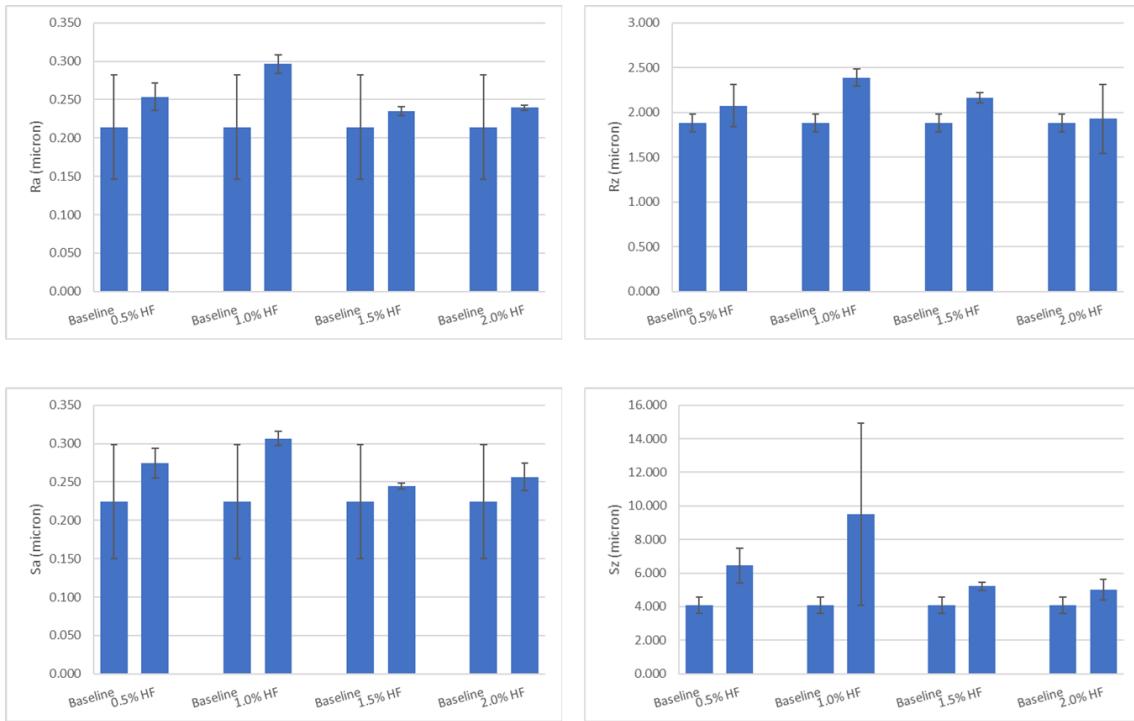


Figure 21. Comparison of the Ra, Rz, Sa, and Sz values before and after etching for Etch Set 2 samples etched for the duplicate in 30% HNO_3 and varying concentrations of HF. Each etch lasted for 20 seconds.

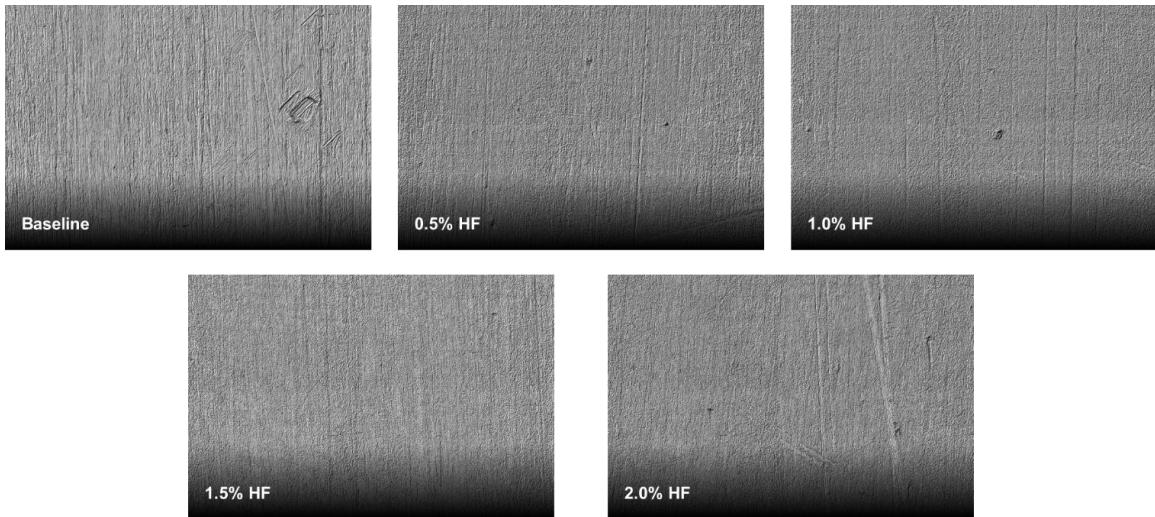


Figure 22. C-DIC images at 20x magnification from etched Set 2 samples from the duplicate testing at 30% HNO_3 and varying concentrations of HF. Each etch lasted for 20 seconds.

For the third flash etching test (Set 3), the concentrations of the solutions remained the same, but the etch time was increased to 40 seconds. Images of the Zr metal squares following the 40 second etch are shown in Figure 23. The data comparison for each sample and the baseline for the 40 second etch are shown in Figure 24. The 20x magnification C-DIC images are shown in Figure 25. The surface roughness changes at 2 wt% HF were not as significant as they were at the lower concentrations with the increased time and the surface appears brighter. Staining was still present on all samples.



Figure 23. Set 3 samples etched at 30 wt% nitric and varying hydrofluoric concentrations compared to a color chart. Etch time was for 40 seconds.

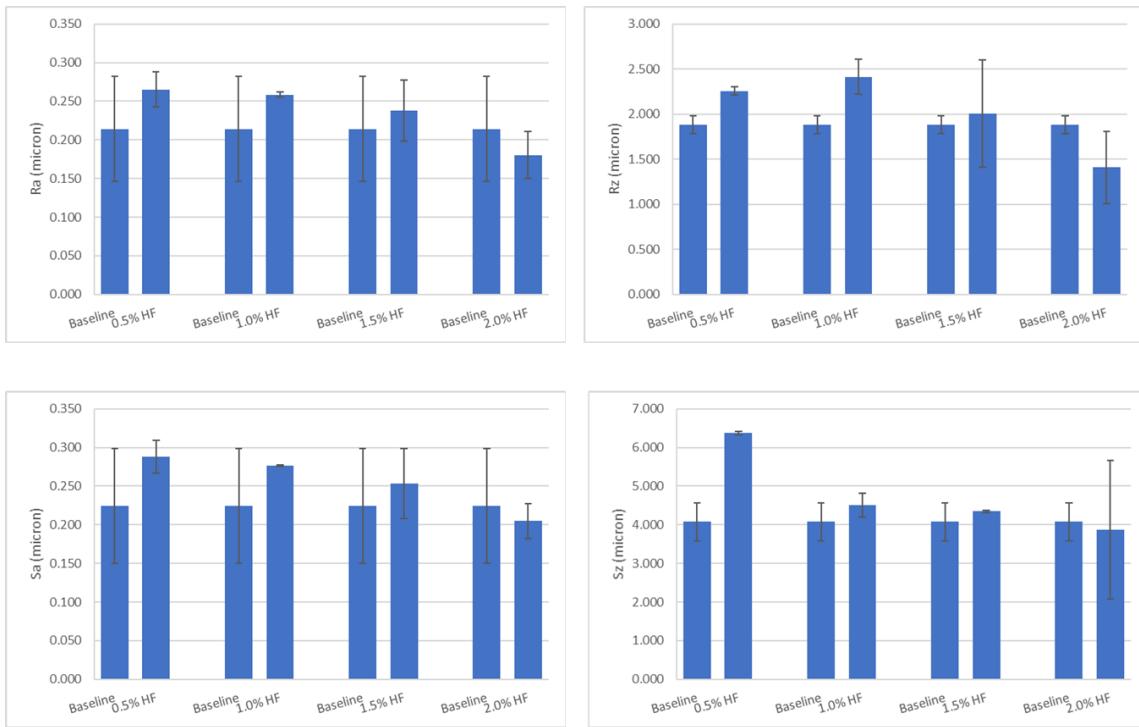


Figure 24. Comparison of the Ra, Rz, Sa, and Sz values before and after etching for Set 3 samples etched in 30% HNO_3 and varying concentrations of HF. Each etch lasted for 40 seconds.

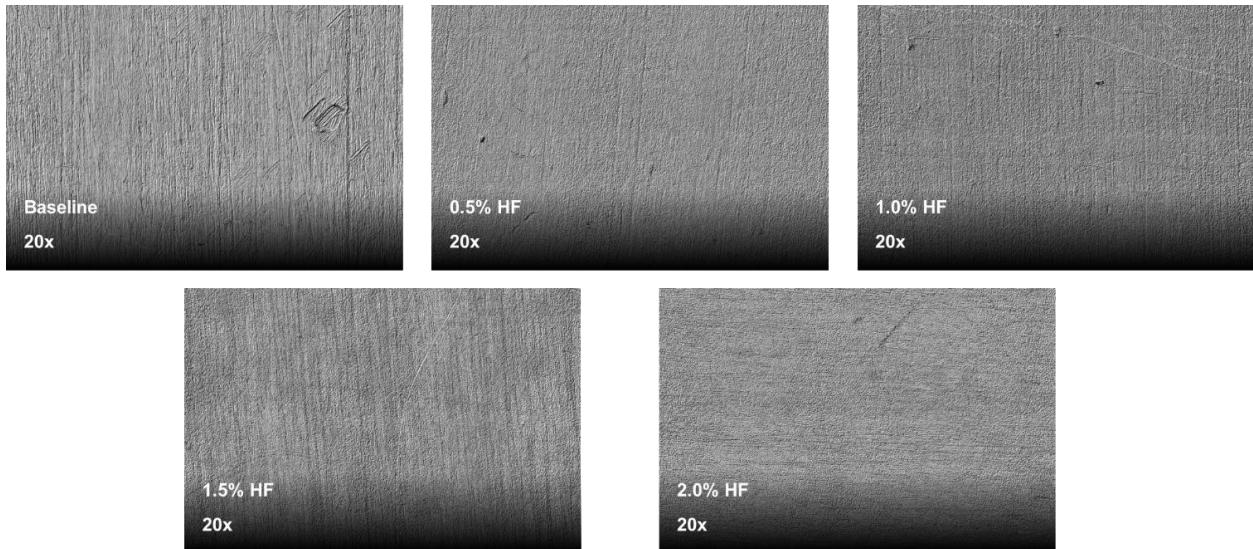


Figure 25. C-DIC images at 20x magnification for Set 3 samples etched in 30% HNO_3 and varying concentrations of HF. Each etch lasted for 40 seconds.

Measured mass changes from the repeated 20 second etch study and this test are shown in Table 2. The mass loss increased with increasing HF concentration and was larger for the 40 second etch samples than the 20 second samples, resulting in variable dimensional removal.

Table 2. The mass changes for the 20 second and 40 second etches in 30% HNO_3 with varying concentrations of HF.

Etch Time	HF Wt %	Initial Mass (g)	Final Mass (g)	Mass Difference (g)
20 Seconds	0.5	4.859	4.846	0.013
	1.0	4.932	4.908	0.024
	1.5	4.909	4.866	0.043
	2.0	4.674	4.628	0.046
40 Seconds	0.5	4.908	4.900	0.008
	1.0	4.933	4.914	0.019
	1.5	4.685	4.629	0.056
	2.0	4.476	4.405	0.071

3.3.3 Flash Etch Sets 4 and 5: 40% HNO₃ – Etch Times of 20 Second and 40 seconds

Flash etching test for Sets 2 and 3 were repeated, but the concentration of nitric acid was increased to 40 wt%. Images of the Set 4 post-etch samples, etched at 40 wt% nitric and varying hydrofluoric acid concentrations for 20 seconds is shown in Figure 26. The LCM data for this data set are shown in Figure 27. The 20x magnification C-DIC images are shown in Figure 28, respectively. Surface roughness changes were more significant at lower hydrofluoric concentration while staining is more prominent with increasing hydrofluoric concentration when compared to against the as-manufacture material and baseline hand abrasive polish.



Figure 26. Comparison of the Set 4 post-etch samples and a color chart etched in 40wt% HNO₃ at varying HF concentrations. The etch time was 20 seconds.

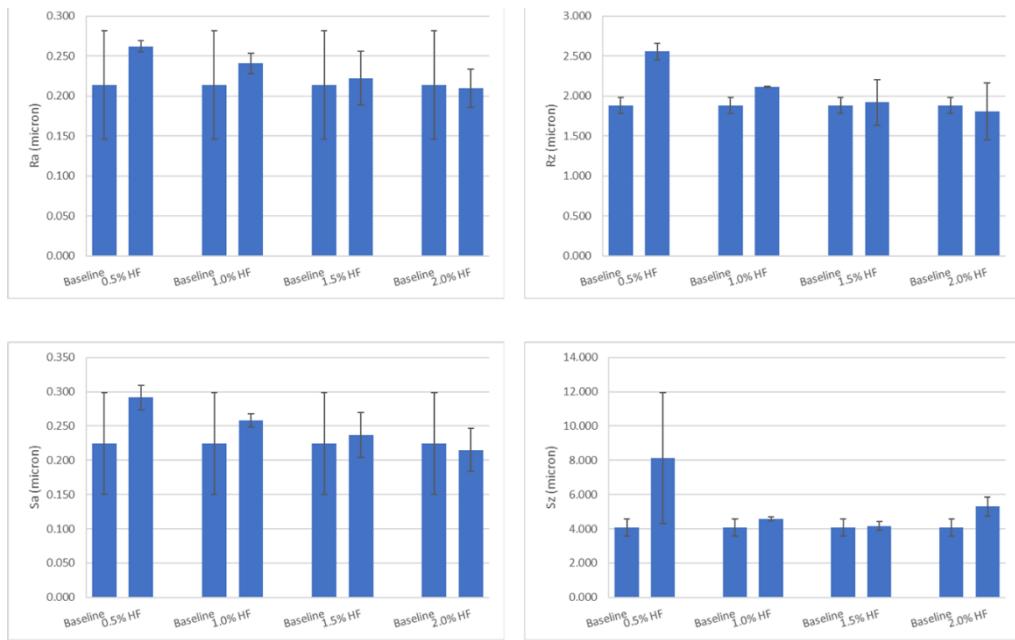


Figure 27. Comparison of the Ra, Rz, Sa, and Sz values before and after etching Set 4 samples etched in 40wt% HNO₃ and varying concentrations of HF. Each etch lasted 20 seconds.

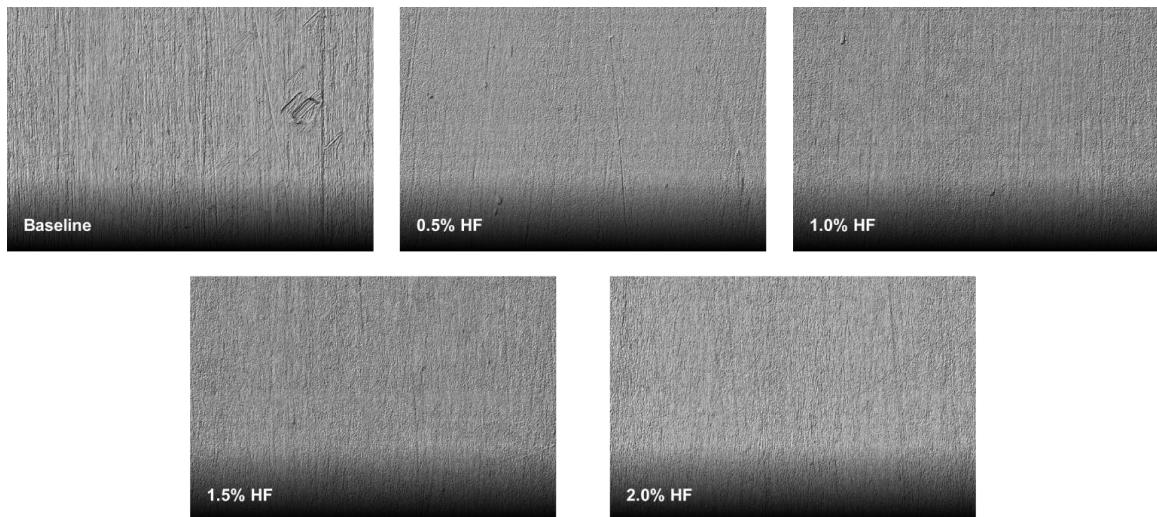


Figure 28. C-DIC images at 20x magnification for Set 4 samples etched in 40% HNO₃ and varying concentrations of HF. Each etch lasted for 20 seconds.

Set 5 zirconium samples etched in 40wt% HNO_3 and varying HF concentrations, but the etch time was increased to 40 seconds. The comparison between each etched square and a color chart is shown in Figure 29. The LCM data for this data set are shown in Figure 30 with the C-DIC images at 20x magnification for each sample are shown in Figure 31. The results are very similar to all the previous test results with staining on the surface that increased with increasing HF concentration.

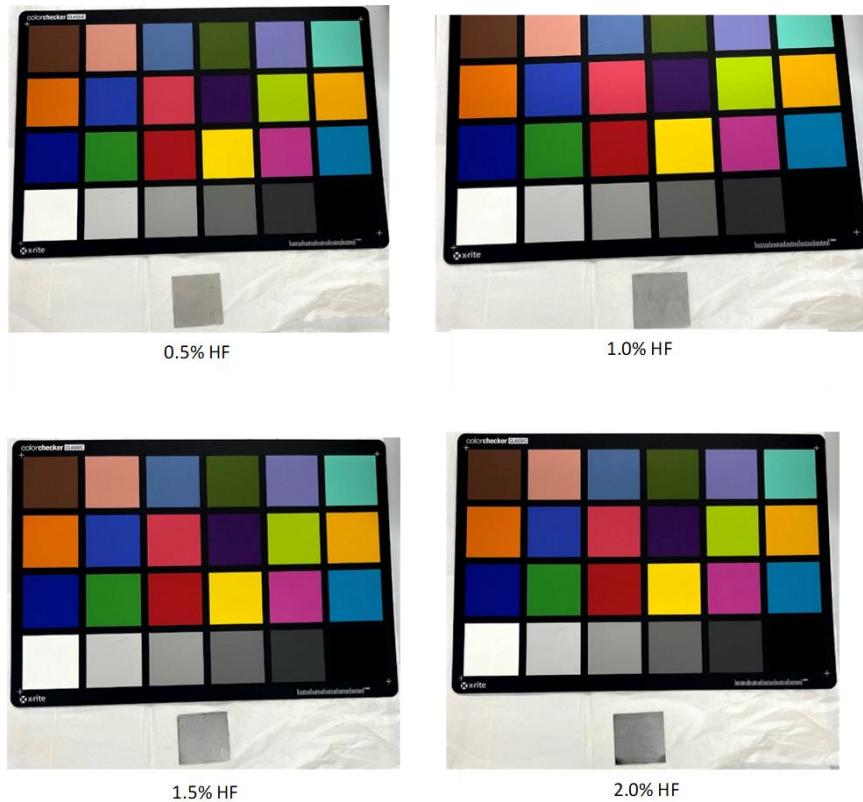


Figure 29. Comparison of the Set 5 post-etch samples and a color chart etched in 40wt% HNO_3 at varying HF concentrations. Etch time was 40 seconds.

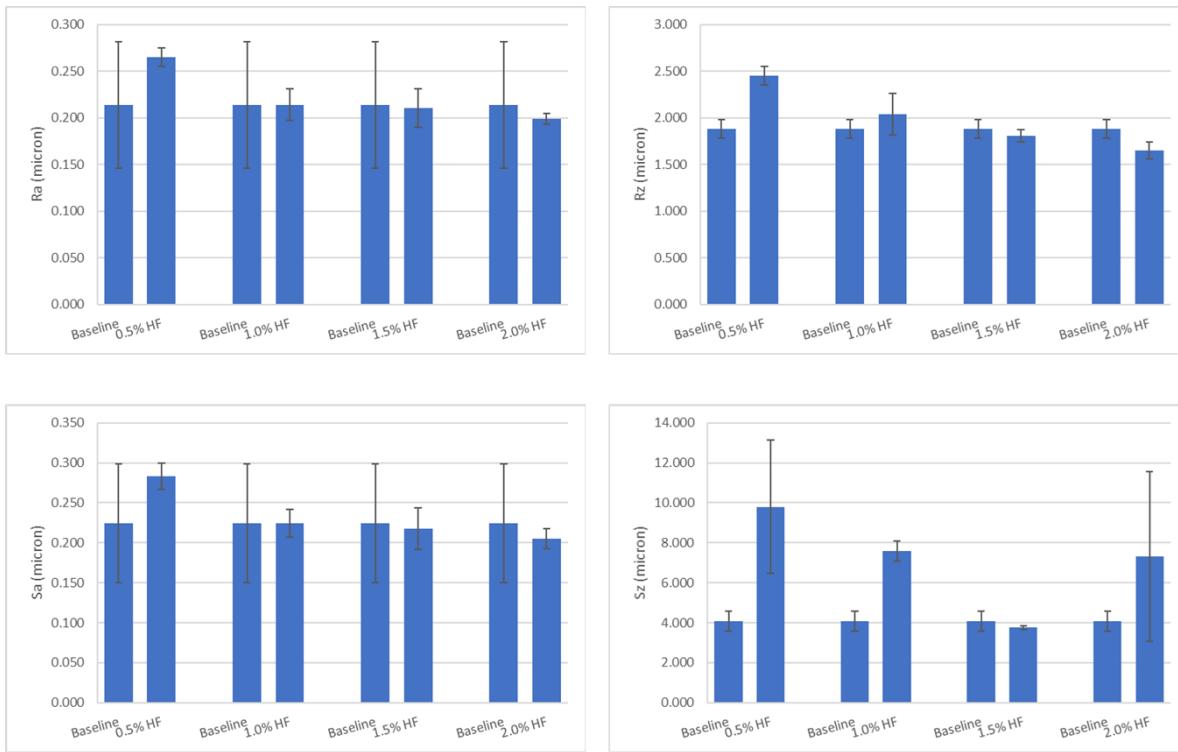


Figure 30. Comparison of the Ra, Rz, Sa, and Sz values before and after the Set 5 were etched in 40wt % HNO₃ and varying concentrations of HF. Each etch lasted for 40 seconds.

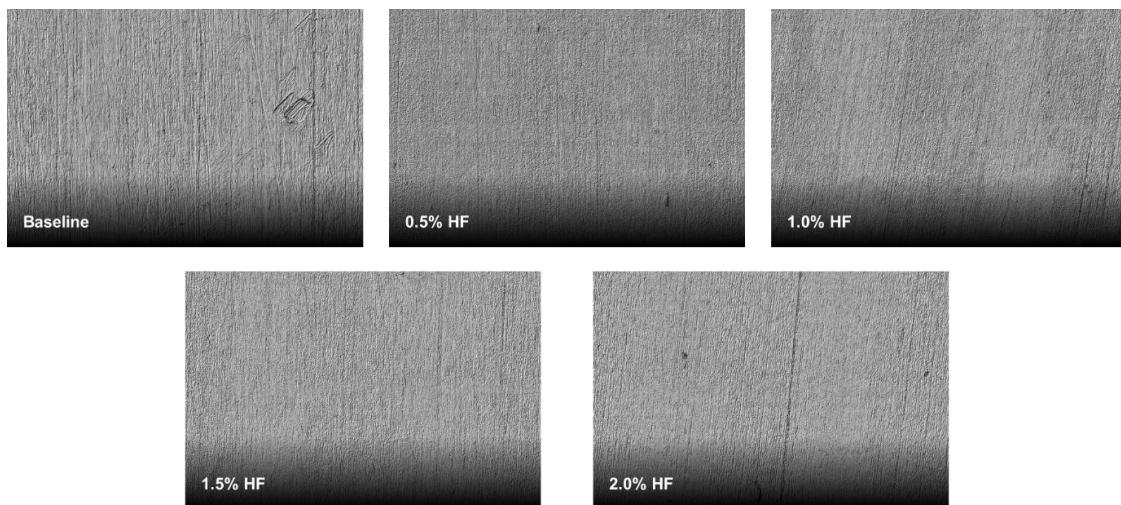


Figure 31. C-DIC images at 20x magnification for the Set 5 samples etched in 40% HNO₃ and varying concentrations of HF. Each etch lasted for 40 seconds.

The mass change for each sample from both the 20 second and 40 second etches is shown in Table 3. Results are very similar to the Table 2 results, indicating the impact to increasing the nitric acid concentration to 40wt% to 30wt% was minor.

Table 3. The mass change for each sample etched in 40% HNO_3 and varying concentrations of HF.

Etch Time	HF Wt %	Initial Mass (g)	Final Mass (g)	Mass Difference (g)
Set 4 20 Seconds	0.5	4.795	4.787	0.008
	1.0	4.733	4.725	0.008
	1.5	4.461	4.437	0.024
	2.0	4.591	4.533	0.058
Set 5 40 Seconds	0.5	4.699	4.671	0.028
	1.0	4.741	4.723	0.018
	1.5	4.661	4.616	0.045
	2.0	4.648	4.566	0.082

3.3.4 Acid Etching Discussion

As the concentration of HF increased, the etch rate increase, more staining was present, and the dimensional loss was more variable. The impacts of etch time and HNO_3 concentration were small. Surface roughness also increased more than what was seen with the baseline process using the abrasive paste. Observed staining from this process is a result of residual acid reacting with the surface upon removal. This results in localized surface oxidation growth which are rich in fluoride and appear brownish and blue from light detraction through the thicker layer. While this was observed on all samples, the limitations of quenching the reaction on the zirconium with sufficient rinse water during removal of the sample from the etching solution in a laboratory environment is likely the cause. The results indicate the importance of quenching this reaction upon removal and how the reactivity of the etching solution plays into that transfer.

3.4 Alcohol Cleaning of Heat-Treated Samples in Contact with Neolube-Coated Steel Plate

Three Zr sheets were heat treated in close contact with Neolube-coated steel plate as described in Section 2.3.1. The three Zr sheets prior to heat-treatment are compared to those heat-treated as shown in Figure 32. No visual difference in the surface appearance was found.

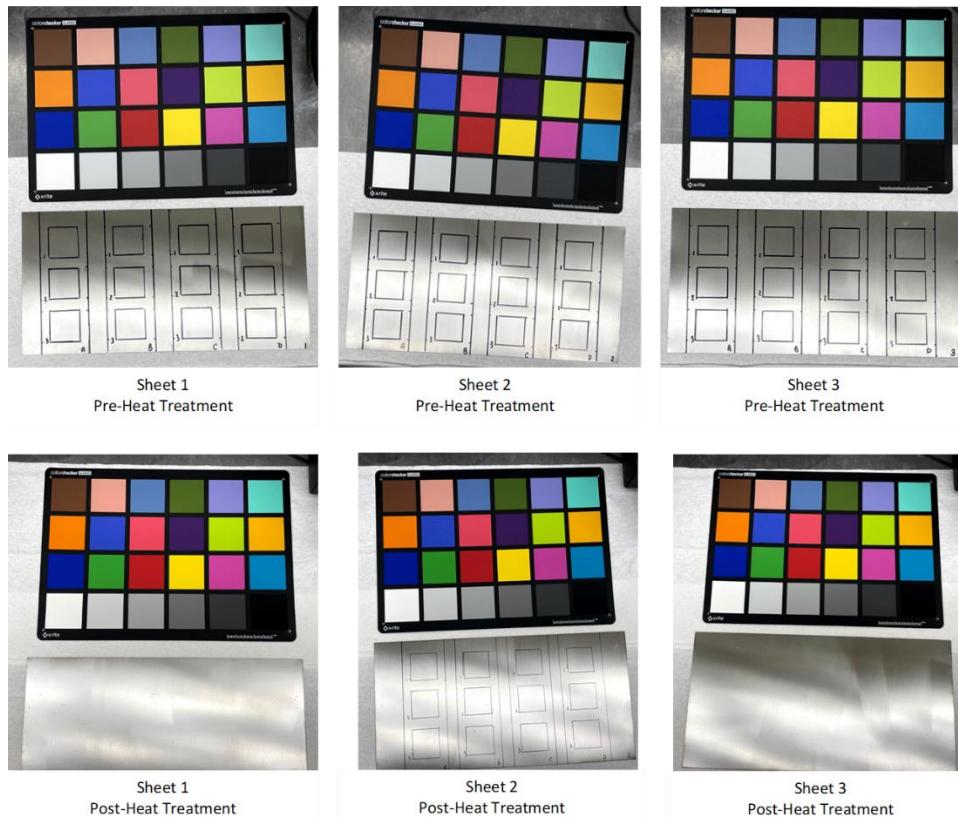


Figure 32. Sheets 1–3 before and after heat treatment between two Neolube-coated, stainless-steel sheets.

Sheet 2 was further analyzed via LCM before and after heat treatment to evaluate possible changes in the surface condition. A data comparison before and after heat-treatment/cleaning on this plate is shown in Figure 33 and C-DIC image comparisons are shown in Figure 34. No significant change to the surface was observed by LCM.

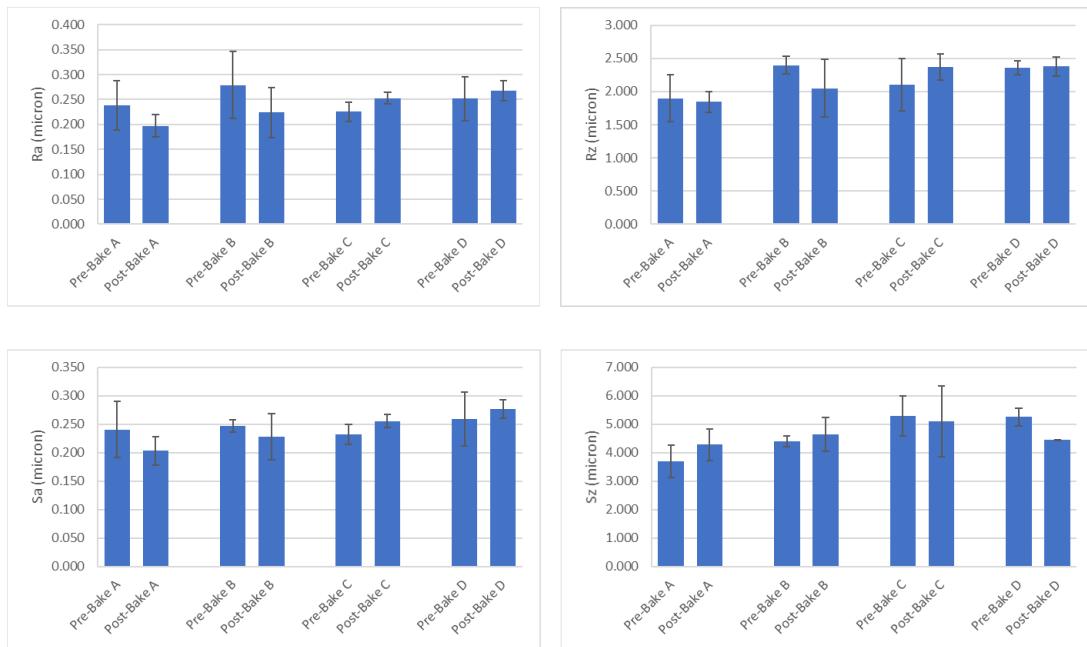


Figure 33. Ra, Rz, Sa, and Sz values for Sheet 2 before and after alcohol cleaning after heat treatment in contact with Neolube.

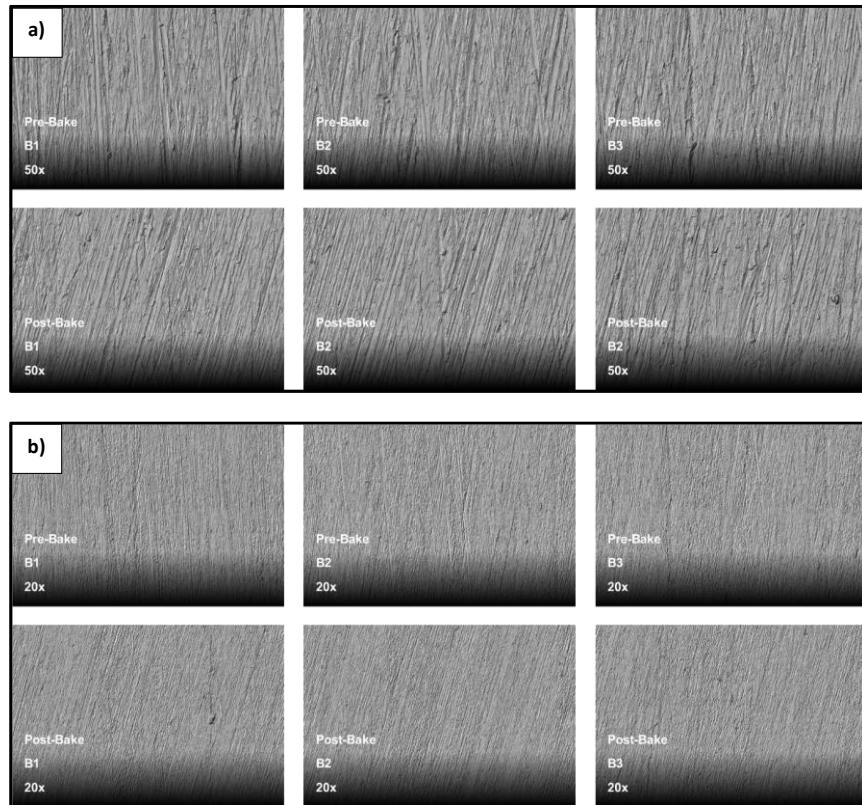


Figure 34. C-DIC images at (a) 50x and (b) 20x magnification of Sheet 2 before and after alcohol cleaning after heat treatment in contact with Neolube.

Sheet 1 was analyzed via XRD, XPS, and SEM to determine if contaminants or inclusions were present on the surface. XRD and XPS indicated the presence of oxygen and carbon on the surface, consistent with the as-received material. SEM images from each location are shown in Figure 35. No inclusions were found on the surface of the heat-treated samples during SEM analysis.

The surface roughness values did not change upon heat treatment and no staining was present on the surface. Overall, the surface quality was not drastically altered after heat treatment indicating the presence of Neolube on the steel plates does not easily transfer to the Zr.

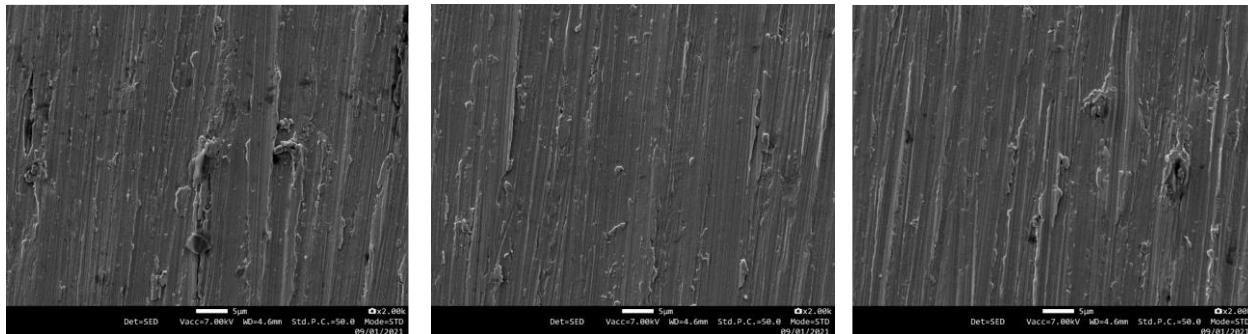


Figure 35. SEM surface images from Plate 2 after alcohol cleaning after heat treatment in contact with Neolube

3.5 Cleaning Zirconium with Neolube Present

The following results describe the analyses described in Section 2.3.3 where Zr samples were coated with Neolube, heat treated, and then cleaned with either ethanol, Scotch-Brite, or acid etch. These tests were used to evaluate the best method remove Neolube on the Zr after the hot rolling and de-canning process.

3.5.1 Ethanol Cleaning

The baseline approach for the decanned foil after hot rolling is to wipe any residual Neolube that may have transferred from the steel can with alcohol. Using the approach described in Section 2.3.2, the plates were cleaned with alcohol. One of strips was characterized afterwards by LCM, XRD, XPS, and SEM. The LCM data before and after heat treatment and polishing are shown in Figure 36. The 10x magnification C-DIC images are shown in Figure 37.

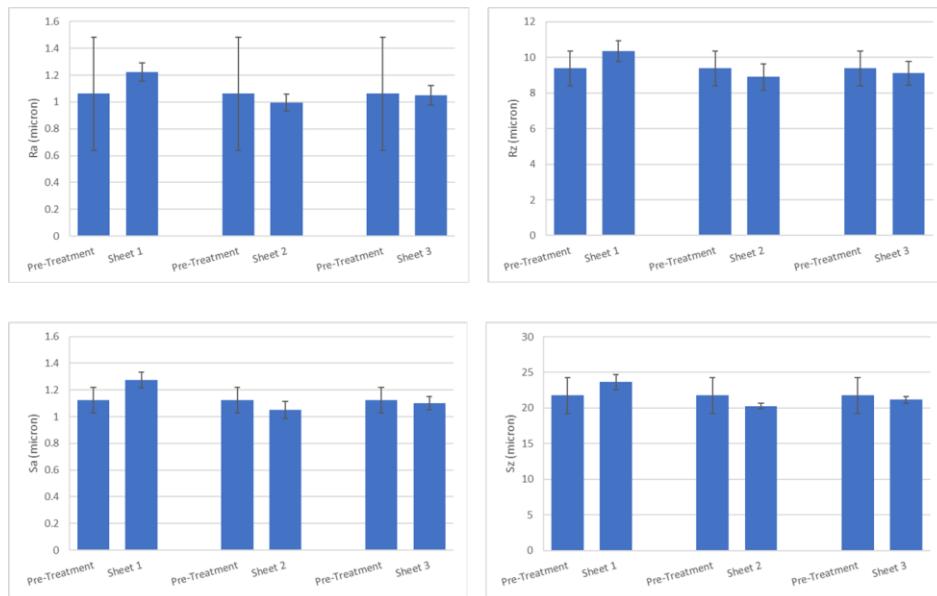


Figure 36. Ra, Rz, Sa, and Sz values for Section A cleaned with ethanol before and after heat treatment and Neolube removal. There was little difference in surface roughness values.

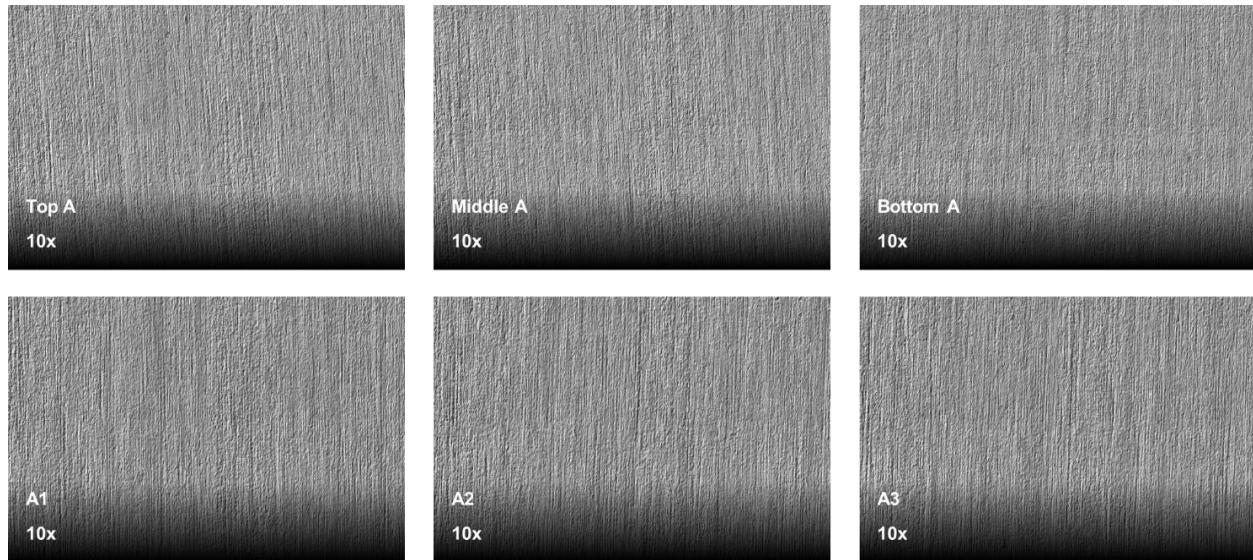


Figure 37. The 10x magnification C-DIC images before and after heat treatment and Neolube removal with ethanol.

The XRD scan data of the surface of the ethanol cleaned samples are shown in Figure 38. The scans indicate carbon compounds present on the surface. XPS analysis indicates the presence of Zr, O, and C, which confirms the information obtained by XRD analysis. However, similar scans by XRD indicate similar patterns on the as-received material as well. SEM analysis of the surface found no sign of carbide inclusions on the surface (Figure 39). SEM imaging of the cross sections indicated an oxide layer with a thickness of between μm 2-4 shown in Figure 40. This is a similar thickness as seen on the as-received Zr samples indicating no significant impact of Neolube presence after the alcohol wipe.

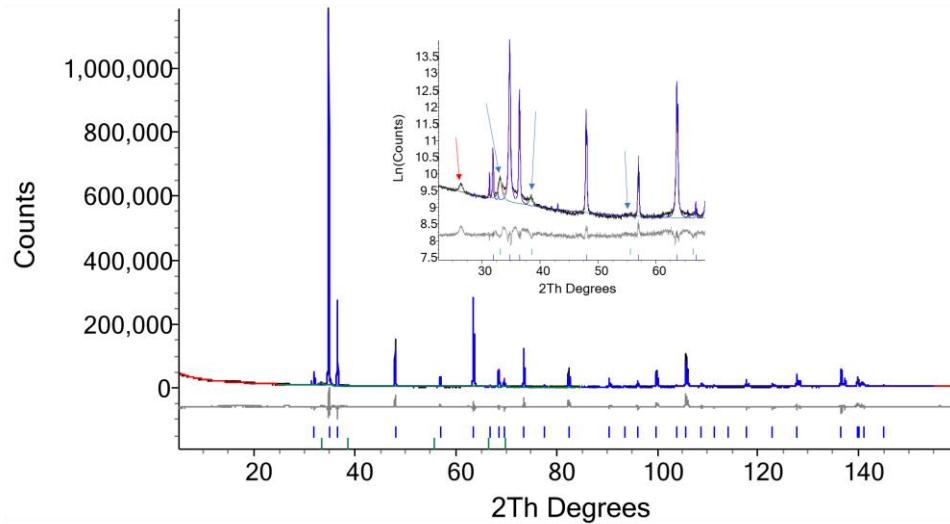


Figure 38. XRD scan of alcohol clean plate heat treated with Neolube on surface. Similar pattern found on as-received material.

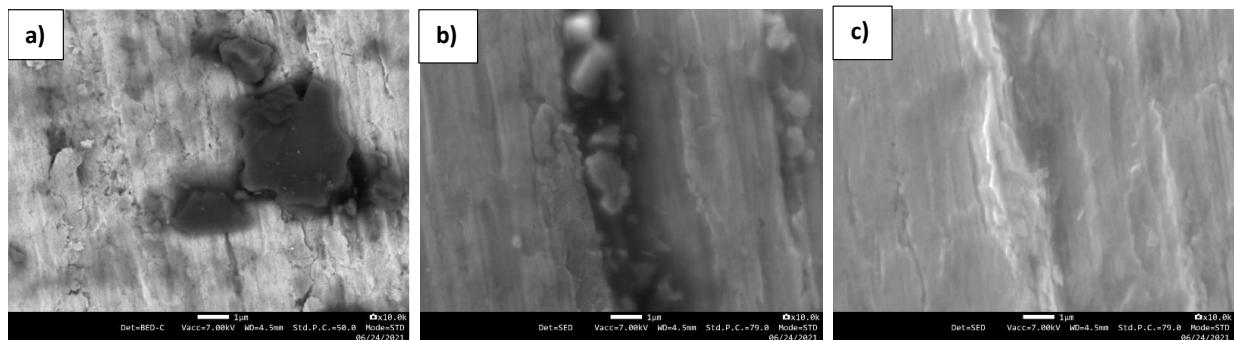


Figure 39. SEM images for the samples cleaned with ethanol. Images a), b), and c) represent three different regions analyzed at 10,000x magnification. These images show no carbide inclusions.

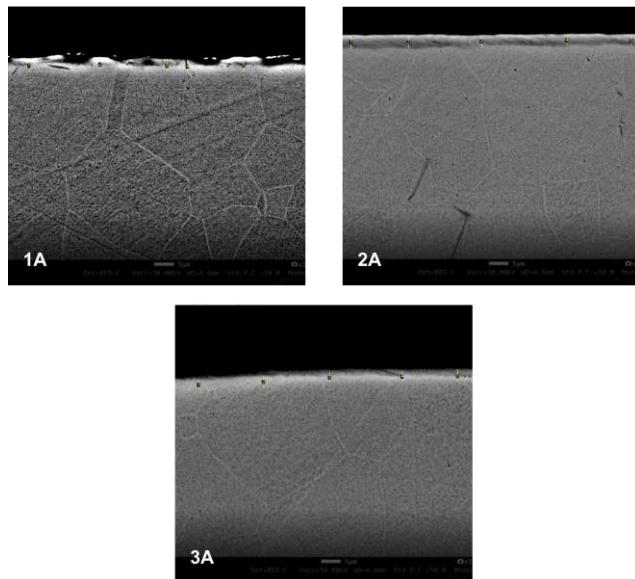


Figure 40. Oxide layers found on the ethanol cleaned sheets

3.5.2 Scotch-Brite™ Polishing

The heat treated Zr samples coated with Neolube were polished using Scotch-Brite™ after alcohol cleaning as described in Sections 2.3.2 and 3.5.1. Two different varieties of Scotch-Brite™ pads were evaluated on the three Zr plates (Figure 41a). The sections from Sheets 1 and 2 were polished with the Final Stripping (Green Fine Grade) pads, and the section from Sheet 3 was polished with the Ultra Fine Grade Gray Hand Sanding pad. Figure 41(b) shows the initially results for polishing the top third of the strip, and Figure 41(c) shows the final finish. Like hand polishing with the diamond abrasive paste, this method was found to be labor intensive and difficult to reach the edges of the plates. After polishing, the plates were again hand cleaned with alcohol and then analyzed via LCM, XPS, XRD, and SEM.



Figure 41. Scotch-Brite Pads (a) used for cleaning. Strip C1 before (b), during (c), and after cleaning (d).

An LCM data comparison is shown in Figure 42 for all three sheets. Sheets 1 and 2 polished with the green Final Stripping for Residue Removal pads showed an increase in surface roughness while Sheet 3 polished with the Ultra Fine Gray Hand Sanding pad showed a decrease in surface roughness as compared to before treatment. However, the changes are only minor, and the surface not significantly improved over the material prior to treatment. The 10x magnification C-DIC images for Sheet 1 (Fine Grade) are shown in Figure 43 and Sheet 3 (Ultra Fine Grade) in Figure 44, which show no significant change before and after polishing from either grade of Scotch-Brite™ pad.

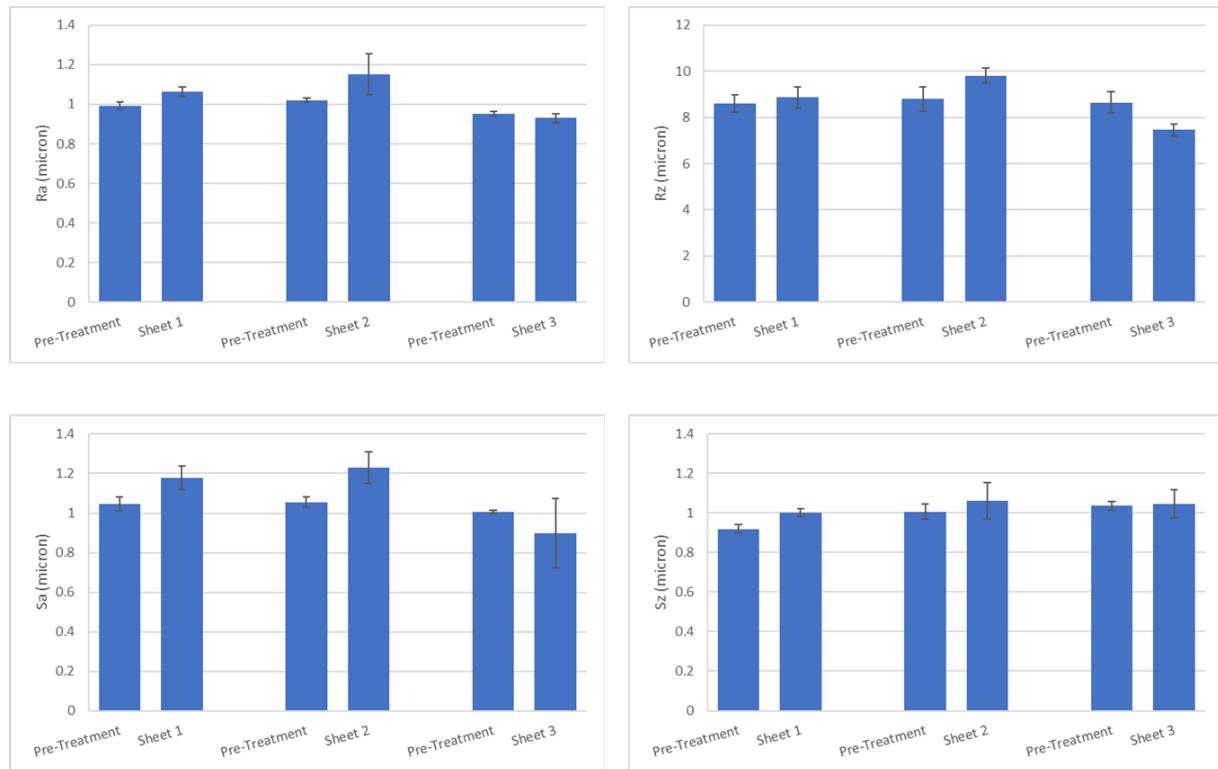


Figure 42. Comparison of the Ra, Rz, Sa, and Sz values before and after polishing with Scotch-Brite™ to remove residual Neolube on surface of heat-treated zirconium.

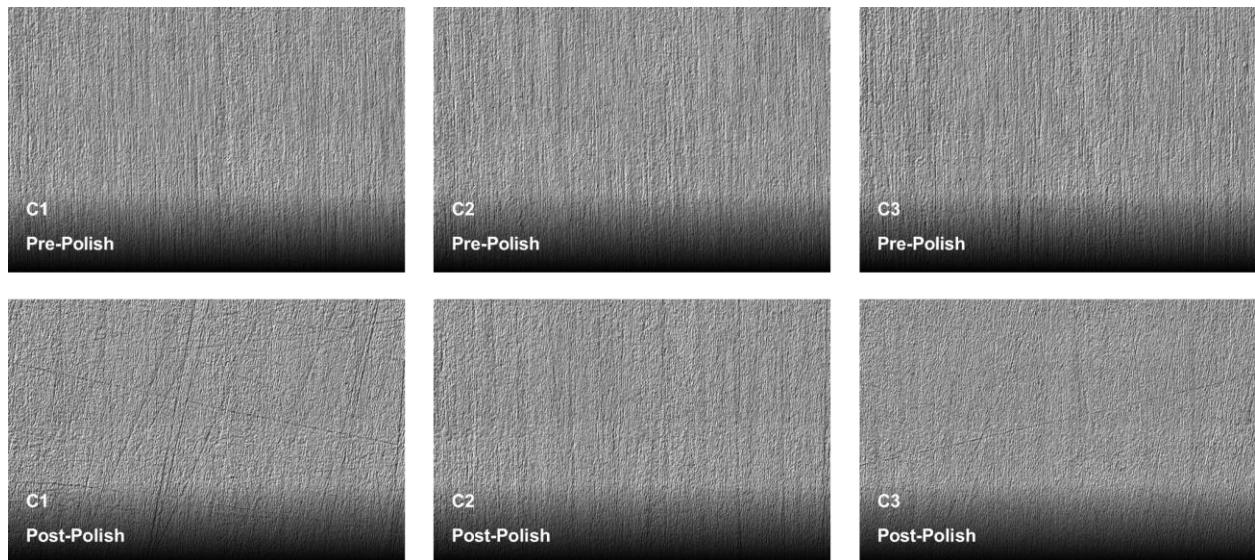


Figure 43. The 10x magnification C-DIC images for Section C from Sheet 1 before and after polishing with the Green Fine Grade Scotch-Brite pads to remove residual Neolube on surface of heat-treated zirconium.

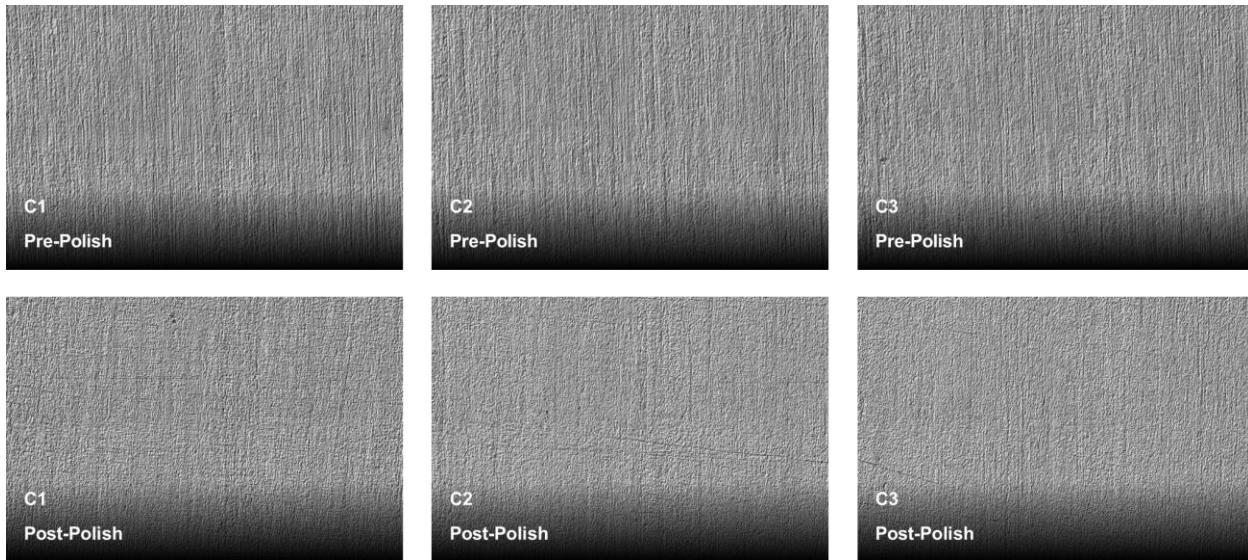


Figure 44. The 10x magnification C-DIC images from Section C of Sheet 3 before and after hand polishing with the Ultra Fine Scotch-Brite™ pad to remove residual Neolube on surface of heat-treated zirconium.

XRD analysis data found of carbon compounds on the surface like that found on the received plate. The XPS analysis (Figure 45) found carbon present as well along with an oxide layer on the polished plate. XPS also found indications of trace amounts of nitrogen on some of the plates, which is present in the nylon backing of the pads.

The SEM surface scans and found no carbide inclusions present. However, imbedded grit particles on the surface are shown in Figure 46, which is a concern when implementing a dry polishing method. Oxide layers were found on the surface of by SEM inspection of the plate cross sections as shown in Figure 47. Thickness measurements were between 2 to 5 μ m, similar to the other measurements performed.

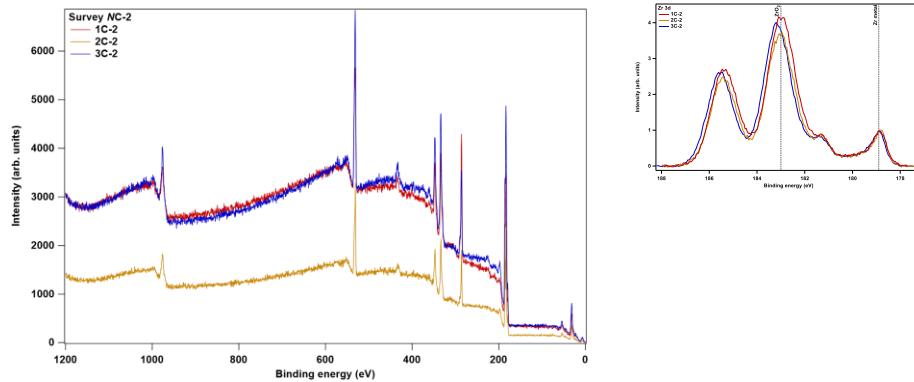


Figure 45. XPS scans of hand polished surface using Scotch-Brite™ pad to remove residual Neolube on surface of heat-treated zirconium.

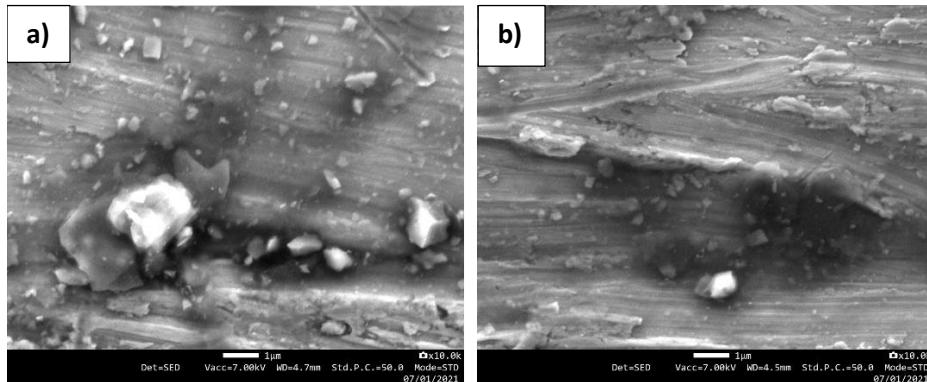


Figure 46. SEM images for samples polished using Scotch-Brite™ pads. Images a) and b) represent locations analyzed at 10,000x magnification.

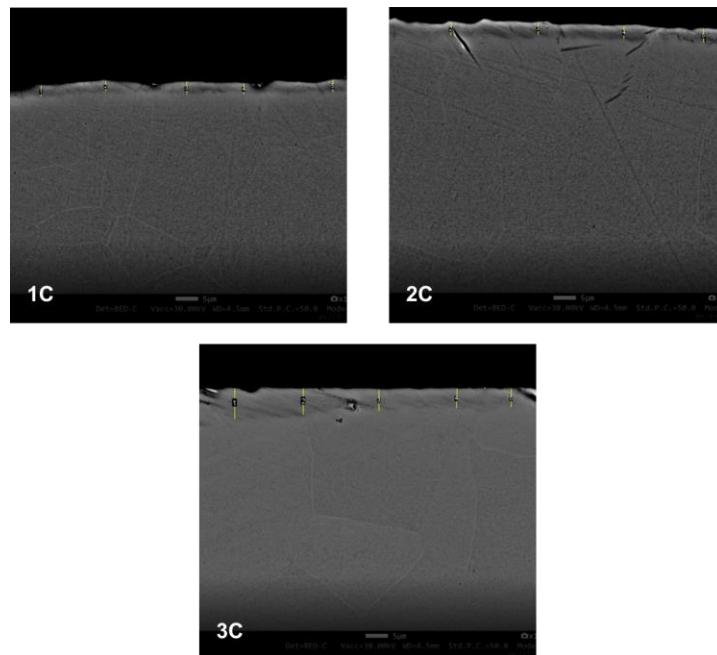


Figure 47. SEM images for the Scotch-Brite™ polished sheets. An oxide layer is visible on each sheet.

Overall, the surface roughness was not significantly impacted by either of the grades of Scotch-Brite™ pads. This method also left grit from the Scotch-Brite™ pads on the surface, even after cleaning with alcohol. This cleaning process required significant effort for minimal changes in surface quality and is not recommended for further use.

3.5.3 Flash Etching

The final technique used to remove the Neolube after heat treatment was flash etching with nitric acid and HF as described in Section 2.3.2. After measurement of the surface area was completed after alcohol cleaning, on plate was cut into 1" strips and flash etched into a 3 wt% HF / 30 wt% nitric acid solution by immersion as shown in Figure 48a and Figure 48b. The remaining Neolube on the surface was quickly removed but the graphite in the lubricant did not dissolve and stayed on the surface of the etchant and rinse water used, leaving a "bath-tub" ring on the containers afterwards as shown in Figure 48c. Comparison of the surface afterward to the pre-etched surface shows improvement (Figure 48d), but staining was an issue (Figure 48e) due to the lack of rinse water working in a laboratory environment as discussed in Section 3.3. While immersion etching presents some operational challenges (lubricant not dissolving, staining of surface), the lubricant readily lifts off the surface using the etchant. Also, immersion cleaning would likely not use immersion cleaning after hot-rolling with the U-10Mo at the edges. Instead, a commonly used reworked method called "spot etching" could be used. This method uses a cotton swab soaked in etchant to remove stains and contaminants on the surface and quickly rinsed off with a water-soaked cotton rag to remove etchant and other lifted materials off the surface. This method could likely be used to remove small instances of residual contamination on the surface of zirconium with high amount of success.

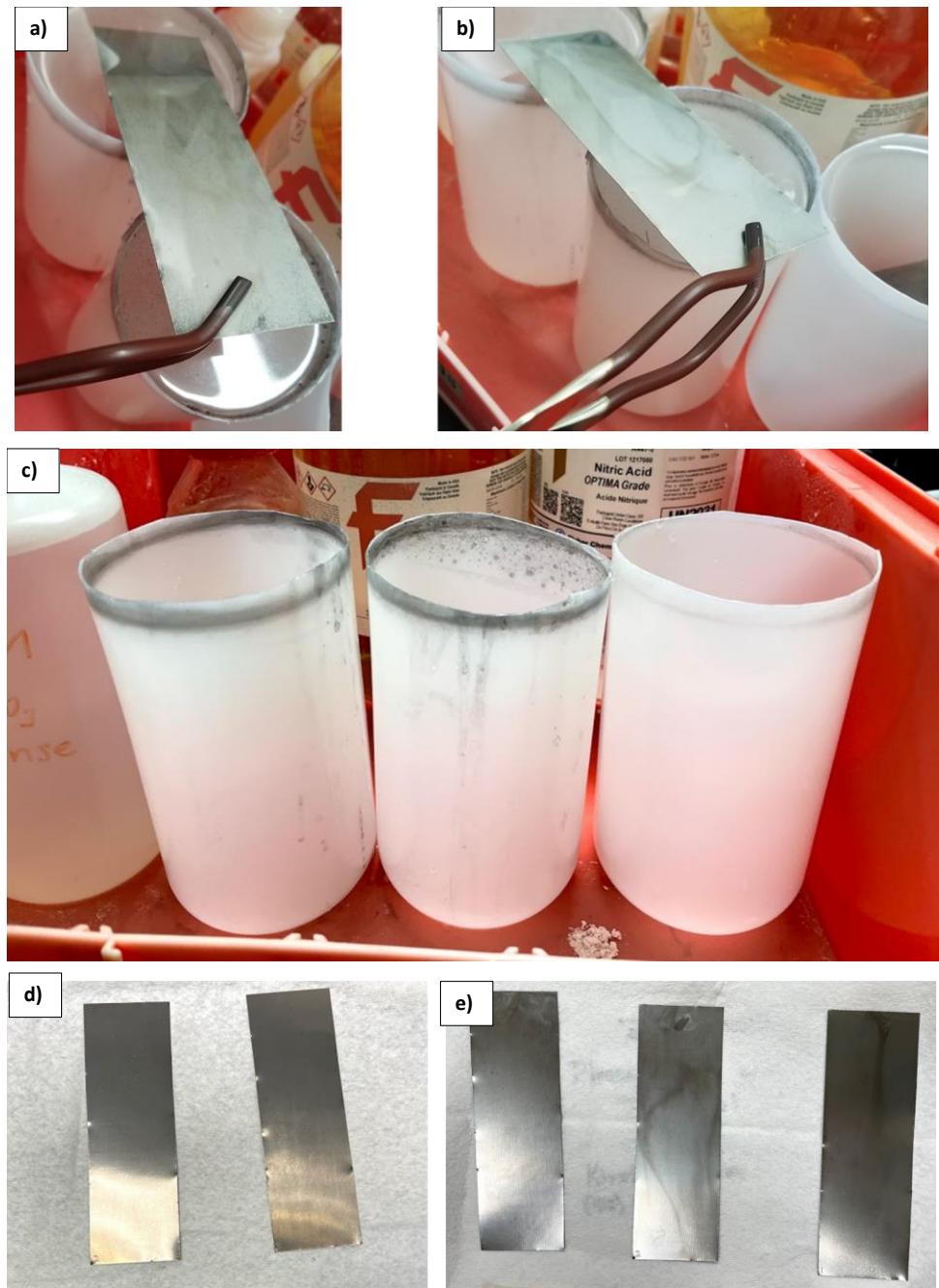


Figure 48. The flash etching process for removing residual Neolube from heat-treated zirconium.

Note: Images (a) and (b) showing strips of heat-treated zirconium being immersed in etchant. Image (c) show the etchant and rinse container with a Neolube bath-tub ring after cleaning. Image (d) compare surface of an etched 1" strip and a non-etched strip, and Image (e) shows the surface of three strips etched side by side.

Following flash etching, each sheet was analyzed via LCM, XRD, XPS, and SEM. The data obtained via LCM are shown in Figure 49 which indicates there was not a significant change in the surface roughness pre- and post-etch. The 10x magnification C-DIC images are shown in Figure 50. Some of the scratches on the surface visually look wider, but the LCM data indicates that the average depth of the scratches were not significantly changed.

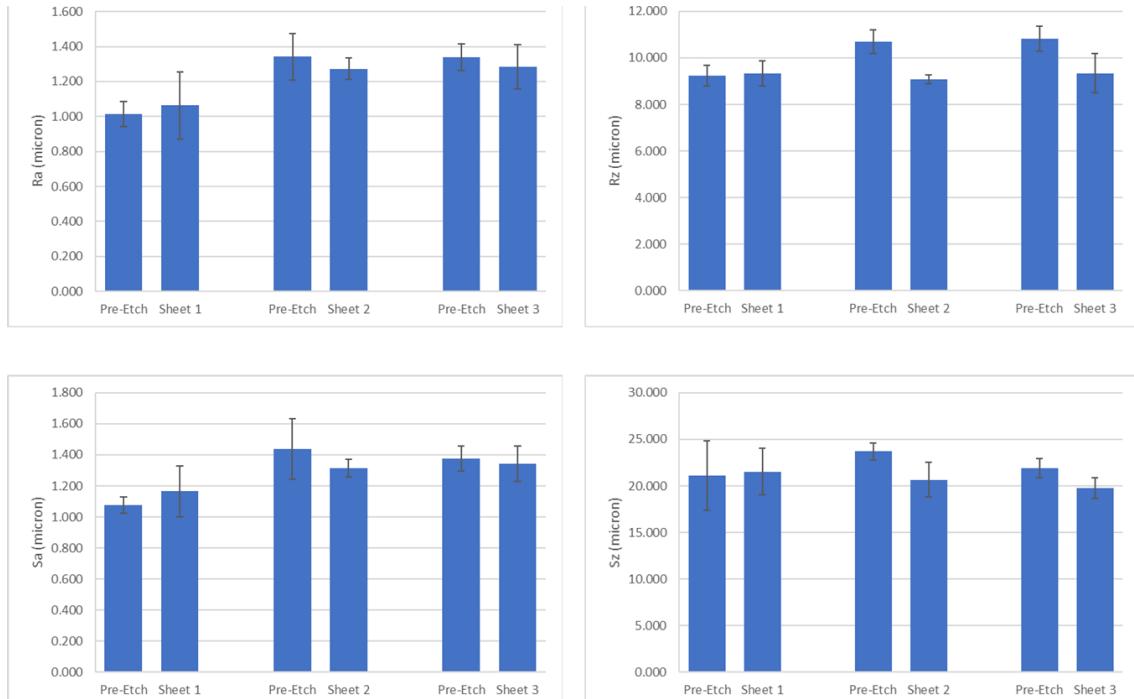


Figure 49. Comparisons of the Ra, Rz, Sa, and Sz values before and after flash etching with HF/nitric acid mixture to remove residual Neolube on surface of heat-treated zirconium.

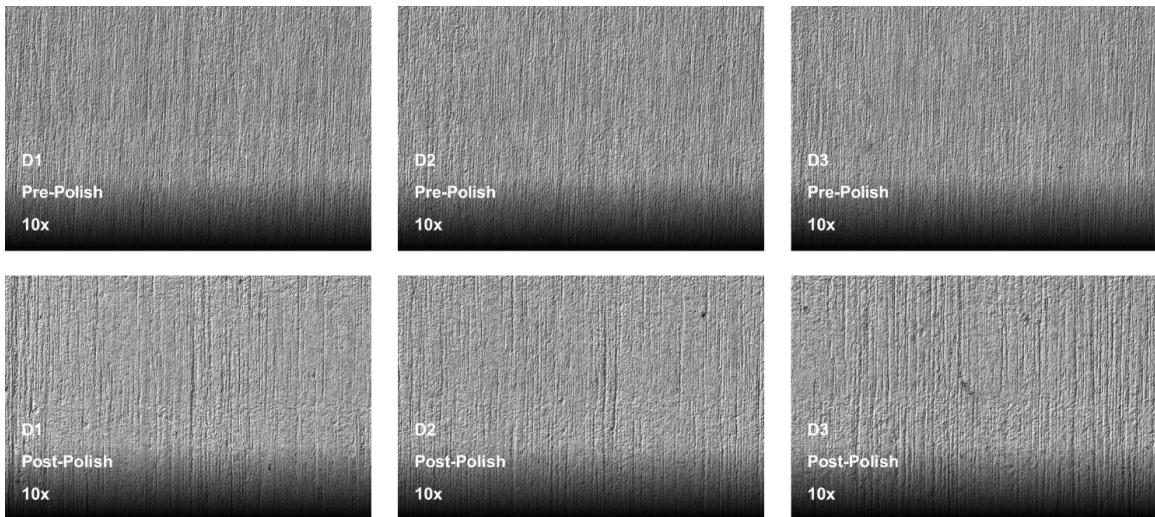


Figure 50. The 10x magnification C-DIC images before and after flash etching with HF/nitric acid mixture to remove residual Neolube on surface off heat-treated zirconium.

Note: The top row represents the sheet prior to etching and the bottom row represents the sheet after etching.

The XRD data and XPS analysis did not find any traces of carbon on the surface, unlike the other testing performed. However, XPS analysis (Figure 51) found strong indications of fluoride present, likely from the use of hydrofluoric acid in the etchant. XPS also found strong indications of a zirconium oxide layer present with a noticeable shift in the binding energy when compared to the other oxide layers detected (Figure 51). The shift is believed to be caused by the presence of fluoride in the oxide layer.

SEM images of the surface (Figure 52) found the surface free of any carbide inclusions. Comparison with the polished surfaces show differences from the etch, with a “cratered” appearance that comes from the generation of gas on the surface from the etchant, versus the “scratched” surface seen from abrasive media. SEM examination of the cross-sections of the surface (Figure 53) indicate an oxide layer was present like other cleaning methods, supporting the XPS findings.

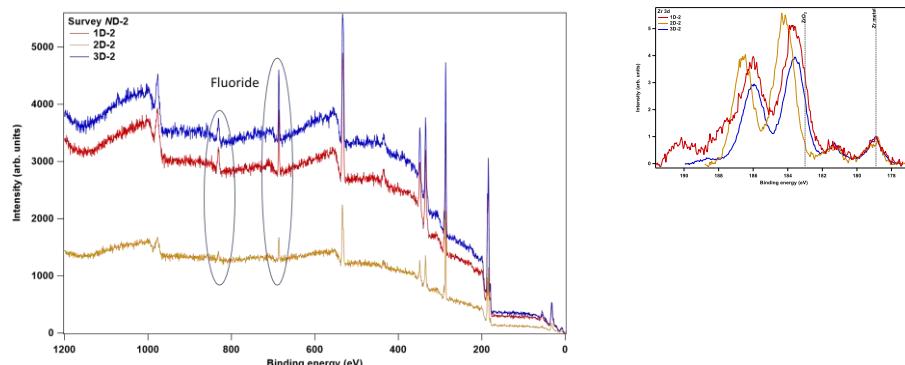


Figure 51. XPS scans of flash etched heat-treated zirconium using HF/nitric acid mixture to remove residual Neolube from surface.

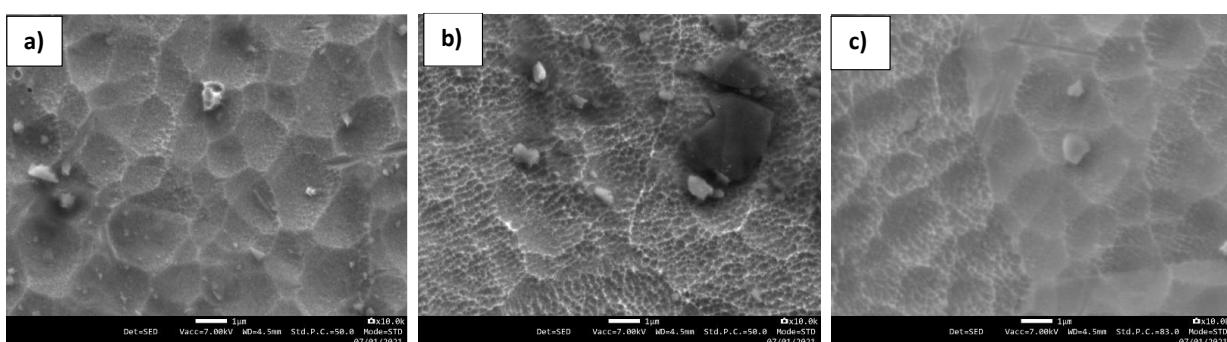


Figure 52. SEM images for etched samples. Images a), b), and c) represent the three locations imaged at 10,000x magnification. No inclusions were found on the surface.

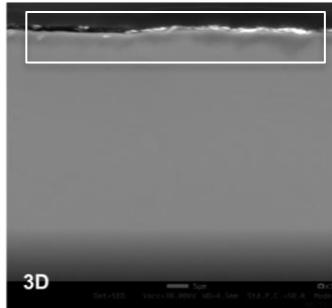


Figure 53. The SEM images for the cross sections of the flash etched sample with indication of oxide layer present.

In summary, flash etching successfully removed the Neolube but did not dissolve the graphite component of the lubricant. While this presents challenges for immersion cleaning, this method would not be utilized for hot-rolled zirconium on the U-10Mo due to the exposure of the uranium at the edges of the rolled plate. A better method for using this technique would be to spot etch where Neolube still sticks to the surface. Analysis of the surface after flash etching found no carbon compounds present but instead, strong indication of fluoride. No carbide inclusions on the surface were seen by SEM but the presence of an oxide layer similar in size to other cleaning methods. XPS confirmed the presence of an oxide layer as well with fluoride present on the surface. While no significant surface roughness changes were seen in this study, surface roughness reduction were seen in the HF/Nitric etching performed in Section 3.3.

3.6 Comparison of Zirconium Cleaning Test Results and Operational Considerations for Implementation

A comparison of the zirconium cleaning results tested are summarized in Table 4, along with operational considerations that should be considered, such as:

- Cost of cleaning: Material, equipment, and labor costs
- Repeatability: How robust is the process and can it be consistently performed?
- Waste generation: Are the cost within reason for needs of cleaning process and does a waste stream exist currently.

Overall, each of the methods have positive and negative associated with that need to be weighed against the operational needs of BWXT. The main things to consider from each of the processes tested are:

- While hand polishing with the Amplex Diamond paste is inexpensive for material costs, it is very labor intensive and difficult to perform at the edge of the zirconium sheets which can cause problem the paste is not removed completely. And while the surface appearance looks good, close-up examination found abrasive inclusions in the metal surface left behind.
- Hand polishing with Scotch-Brite™ pad produced similar results to the diamond paste and presented the same labor issues, difficulty cleaning the edges of material, and having abrasive inclusions found imbedded in the surface after cleaning.
- Wet polishing with abrasive belts performed consistently and produced the most even surface with the least amount of labor without leaving the abrasive inclusions found with dry polishing methods. However, the implementation (equipment, waste stream) cost would be large it is not clear it is necessary for this operation. However, the benefits of receiving polished zirconium versus cleaning in-house should be considered if the cost is reasonable.
- Acid flash etch slightly increases surface roughness, but does not have many of the contamination concerns that the other methods had. However, fluoride was found on the surface of the material due to how hydrofluoric acid dissolve the zirconium metal into solution. There are also high costs associated with using hydrofluoric acid with equipment and waste processing, but the process and treatment of the waste stream is understood by BWXT and exists already at their facility.
- None of the processes tested, including the baseline diamond paste method, completely removed the oxide layer and all methods tested were comparable in surface roughness to each other. Zirconium is a refractory metal and readily absorbs oxygen from air and water to produce a thin oxide layer on the surface, so it is unlikely that any method can remove the oxide layer completely unless it is performed in an oxygen deficient environment. If the original purpose of the cleaning operation was to remove the oxide layer of the zirconium prior to rolling to improve the bond strength, the goals of the cleaning operation should be closer examined since the baseline process does not appear to do this.

Table 4. Summary of Zirconium Cleaning Test Results

	Hand Polishing with Diamond Paste (Baseline)	Mechanical Wet Polishing with Trizact™ Belts	Flash Etching with Nitic Acid/HF and Water Rinse	Scotch-Brite™ Dry Hand Polishing
Visual Appearance	Metallic Bright Finish	Metallic Bright Finish, Staining from Coolant	Matte Finish with Brown Staining	Metallic Bright Finish
Surface Roughness Change	No Change	Belt Dependent	Slight Increase	No Change
Oxide Removal	No Change	No Change	No Change	No Change
Surface Contamination	Silicon, Nitrogen	Sulfur	Fluoride	Nitrogen
Surface Inclusion	Abrasive Grit	None	None	Abrasive Grit
Operation Costs	Labor Intensive	Equipment and Belts	Equipment to store and use HF acids	Labor Intensive
Repeatability	Operator Dependence to Polish Edges Correctly	Consistent Removal and Appearance	Some Operator Dependence to Prevent Staining	Operator Dependence to Polish Edges Correctly
Waste Costs	Low – waste path established	Treatment of waste coolant and grinder fines	Treatment of waste mineral acid – existing waste path	Low – solid waste of used pads

4.0 Conclusions

A set of alternative Zr cleaning methods were investigated to find an alternate way to improve surface quality and reliability of operations. The following methods were investigated:

- Hand Polishing with Diamond Paste
- Mechanical Wet Polishing with Abrasive belts
- Flash Acid Etching with HF/Nitric Acid
- Scotch-Brite™ Pad Polishing

The surfaces were analyzed via LCM and, in some cases, XPS, XRD, and SEM. Ultimately, there were no improvements in surface roughness, and often the method did not remove the carbon contamination seen in the as-received material. The acid etches could remove the carbon contamination and reduce the oxide layer. However, all etches exhibited brown staining on the surface, and the flash etch samples were contaminated with fluoride. Most surfaces did not have inclusions, but grit remaining from the hand polishing and Scotch-Brite™ polishing was found via SEM. An oxide layer also remained on all sheets so the purpose of the cleaning should be re-examined.

Overall, none of these methods had major impacts on the surface characteristics of Zr sheets. This would indicate that the additional effort in diamond polishing the surface, or for that matter any of the other techniques for cleaning the as-received Zr may not be warranted. As for the Zr surface after hot rolling and de-canning, the alcohol wipe approach done currently is sufficient. However, if there are spots of Neolube present on the surface, a flash etching is recommended for spot cleaning as necessary.

5.0 Quality Assurance

This work was performed in accordance with the Pacific Northwest National Laboratory (PNNL) Nuclear Quality Assurance Program (NQAP). The NQAP complies with the United States Department of Energy Order 414.1D, *Quality Assurance*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application* as its consensus standard and NQA-1-2012 Subpart 4.2.1 as the basis for its graded approach to quality.

This work emphasized acquiring new theoretical or experimental knowledge. The information associated with this report should not be used as design input or operating parameters without additional qualification.

6.0 References

Hubbard LR, CL Arendt, NJ Lombardo, CK Clayton, and C Lavender 2020. *LEU-10Mo Steady State Fuel-Fabrication Process Description*. PNNL-29971, Pacific Northwest National Laboratory, Richland, Washington. https://www.researchgate.net/publication/342183468_LEU-10Mo_Steady_State_Fuel-Fabrication_Process_Description

Li L, A Fortier, D Ramirez Tamayo, VV Joshi, and A Soulami. 2021. "Minimizing thickness variation in monolithic U-10Mo fuel foil and Zr interlayer during hot rolling: A microstructure-based finite element method analysis." PNNL-SA- 168343, Pacific Northwest National Laboratory, Richland, Washington. (under review by the journal)

Rabin B, M Meyer, J Cole, I Glagolenko, G Hofman, W Jones, J-F Jue, D Keiser Jr, Y Kim, C Miller, G Moore, H Ozaltun, F Rice, A Robinson, J Smith, D Wachs, W Williams, and N Woolstenhulme. 2017. *Preliminary Report on U-Mo Monolithic Fuel for Research Reactors*. INL/EXT-40975, Revision 1, Idaho National Laboratory, Idaho Falls, Idaho.

Pacific Northwest National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354
1-888-375-PNNL (7665)

www.pnnl.gov