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Electrical-Discharge-Machining Contamination Removal from Metal Additively Manufactured Components

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ABSTRACT

The use of an electrochemical dissolution process is shown to remove the recast layer contamination from the surfaces of electrical-discharge-machining cut components, as well as the interior exposed surfaces of the structure. The solution chemistry, cell potential, and exposure time are all relevant interdependent variables. Optimization of the electrode geometry should be made for each type of component. For the case of Cu-Zn recast contamination of 300-series alloy components, surface composition analysis indicates that complete electrochemical dissolution is achieved using a dilute solution of nitric acid (HNO_3). For example, electrochemical dissolution of the Cu-Zn recast is accomplished at 1.2 V cell potential using a 20% nitric solution and an exposure time of 4 h. The use of a nitric acid bath was specifically chosen since it's chemically compatible and will not degrade the host alloy or the component. In sum, an electrochemically driven dissolution process can be tailored to remove of the recast contamination without affecting the integrity of the host component structure and its dimensional tolerances.

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ACRONYMS AND TERMS

Acronym/Term	Definition
AgCl	silver -chloride
AM	additive manufactured
BS	back-scattered
Cr	chromium
Cu	copper
$Cu(NO_3)2$	copper nitrate
Cu-An	copper-zinc
DI	deionized
EBSD	electron back-scattered diffraction
EDM	electrical-discharge machining
EDS	energy dispersive spectroscopy
Fe	iron
FIB	focused ion beam
h	hours
H_2O	
HCl	hydrochloric acid
HNO3	nitric acid
HNO_3	nitric acid
LPBF	laser-powder bed fusion
LSV	linear sweep voltammetry
M	molar
ml	milliliters
Mn	manganese
N_2O	nitrous oxide
O	oxygen
Pt	platinum
RT	room temperature
s	seconds
SE	secondary electron
SEM	scanning electron microscopy
V	volts
Zn	zinc

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1. INTRODUCTION

The complexity of additively manufactured (AMed) metal components has been steadily increasing as the technology continues to mature. Contrary to popular belief, metal AM components do not come out of the machine ready for use and often require additional secondary manufacturing operations before they can be integrated into next-level assembly. During the laser powder bed fusion (LPBF) process, metal powders are melted layer by layer onto a metal substrate (commonly referred to as a build plate) using a high power (~500 W) laser. Typically, following the LPBF step, all components must be removed from the build plate before additional manufacturing operations can proceed. Electrical-discharge machining (EDM) is typically used to remove AM components from the build plate. In the EDM process a wire is elevated to a potential where a discharge current is passed through an electrolytic medium to the component, ablating the material in the path of the wire. During this process, the surface of the wire volatilizes, leaving a recast contamination layer on both the component surface that was cut and on adjacent surfaces. For example, the EDM recast layer consists of a Cu-Zn residue from the use of a brass wire. Historically, EDM recast layers are removed either by mechanical methods like milling or grinding, or by utilizing finer cuts of the EDM wire by using lower voltages that do not necessarily induce brass volatilization.

As AM component complexity has increased in the way of smaller/finer features, the ability to remove the EDM recast layer can become more challenging. Mechanical removal of the layer is no longer feasible when the affected locations cannot be physically accessed by a tool. Additionally, grinding can imbed abrasive particulate into the surface and conventionally machined surfaces induce a depth of damage to the component surface that exceeds the depth of the recast layer, with the potential for stress-induced phase change that can alter the performance of the surface in adverse environments. Finer EDM cuts are also not an option, particularly when the recast products are deposited away from the wire. In sum, traditional EDM recast layer removal methods require "line of sight" access as well as physical space proximate to the affected areas in order to effectively function and may introduce further undesirable contamination. Various methods to address this challenge with particularly complex AM components have been attempted, such as completely avoiding the EDM process by utilizing breakaway supports that allow for components to be mechanically broken off the build plate. However, the viability of such methods for critical nuclear weapon components remains under consideration as the characterization around the impact of such loading during manufacturing on final component functionality in ongoing.

In recognizing this tension between the various aforementioned methods, the technical team supporting AM maturation at SNL/CA in late 2020 realized that a non-mechanical method for EDM recast layer removal needed to be developed. In this report, we describe the development of a novel aqueous electrochemical method for EDM recast layer removal. Post-treatment surface structure and chemical composition were also characterized and documented [1] and were found to be more than acceptable for use in critical nuclear weapon components where tolerance for contamination is limited.

2. CLEANING APPROACHES

As described in Section 1, the authors realized that an aqueous chemical process can be used to dissolve the recast layer. In the current study, 300 series austenitic stainless steels (including 304L and 316L) were considered. The use of a metallographic solution comprised of 55 ml H_20, 60 ml 15.8 M (70%) HNO_3, and 15 ml 0.1 M HCl with a 300 s immersion time and a 1.15 V cell potential provides an electrochemical etch of microstructure for grain boundary relief. For this solution chemistry, HCl is aggressive but buffered in the nitric acid solution; however, the potential exists for uncontrolled dissolution of the host structure as well as the introduction of porosity.

Although the recast layer can be readily removed electrochemically from surfaces that are away from those in direct contract with the EDM wire, it is these EDM-wire cut surfaces that have the highest concentration of EDM recast and the potential for chemical alloying with the Cu-Zn constituents of the EDM from exposure to the plasma during the discharge process. A solution chemistry is desired that removes the Cu-Zn recast but ideally leaves the host structure intact. To dissolve the Cu-Zn recast contamination without aggressive attack of the host 304L or 316L lattice and frame, a dip-immersion using 30% nitric acid was attempted but proved unsuccessful to remove the EDM recast layer as determined by energy dispersive spectroscopy (EDS) measurement. Because 316L is resistant to chemical attack from concentrated nitric acid, an electrochemical process was next pursued to drive dissolution with results described in the remainder of this report.

3. ELECTROCHEMISTY

3.1. Chemical Reactions

Copper (Cu) in the brass recast layer at the EDM-cut surface of the component (and as embedded within the near surface) is oxidized to form copper nitrate $Cu(NO_3)_2$ when exposed to nitric acid HNO_3 as shown in equation (1) for a concentrated solution (>80%) and equation (2) for a dilute solution (<20%). Nitrous N_2O is a gas, and nitrogen dioxide NO_2 is a brownish gas that behaves as an irritant. The balanced reaction for the dissolution of Cu in HNO_3 are shown as follows.

$$Cu + 4 \cdot HNO_3 \rightarrow Cu(NO_3)_2 + 2 \cdot NO_2 + 2 \cdot H_2O \qquad (1)$$

$$4 \cdot Cu + 10 \cdot HNO_3 \rightarrow 4 \cdot Cu(NO_3)_2 + NH_4NO_3 + 3 \cdot H_2O \rightarrow 4 \cdot Cu(NO_3)_2 + N_2O + 5 \cdot H_2O \qquad (2)$$

A similar reaction to equation (2) occurs for zinc (Zn) with the formation of zinc nitrate. In the electrochemical baths used for the dissolution of the EDM-contamination layer, dilute nitric acid baths are used as driven under applied potentials of <2 V. The half-reactions for equation (2) are shown as follows.

$$4 \cdot Cu \rightarrow 4 \cdot Cu^{2+} + 8 \cdot e^{1-} \qquad (3)$$

$$8 \cdot e^{1-} + 10 \cdot HNO_3 \rightarrow 4 \cdot (NO_3^{1-})_2 + N_2O + 5 \cdot H_2O \qquad (4)$$

3.2. Electrochemical Distribution

An electrochemical cell is used to dissolve the Cu-Zn recast contamination layer from the stainless-steel frame using a dilute nitric acid (HNO_3) solution. The Cu-Zn surface layer is dissolved into solution while the host stainless steel frame should remain inert to the bath chemistry. The samples are first cleaned in heated and sonicated aluminum NST cleaner detergent followed by a deionized water rinse. The nitric acid bath was maintained at room temperature (RT) and stirred at 300 rpm. This bath is used for both linear sweep voltammetry (LSV), and constant potential applied to the working electrode (potentiostatic) experiments. A three-electrode electrochemical setup was initially used for the dissolution experiments, consisting of a Ag/AgCl reference electrode, platinum-coated titanium mesh (cathode), and the filter as the working electrode (anode). LSV scans were taken at a 10 $mV \cdot s^{-1}$ scan rate as shown in Figure 1 and Figure 2.

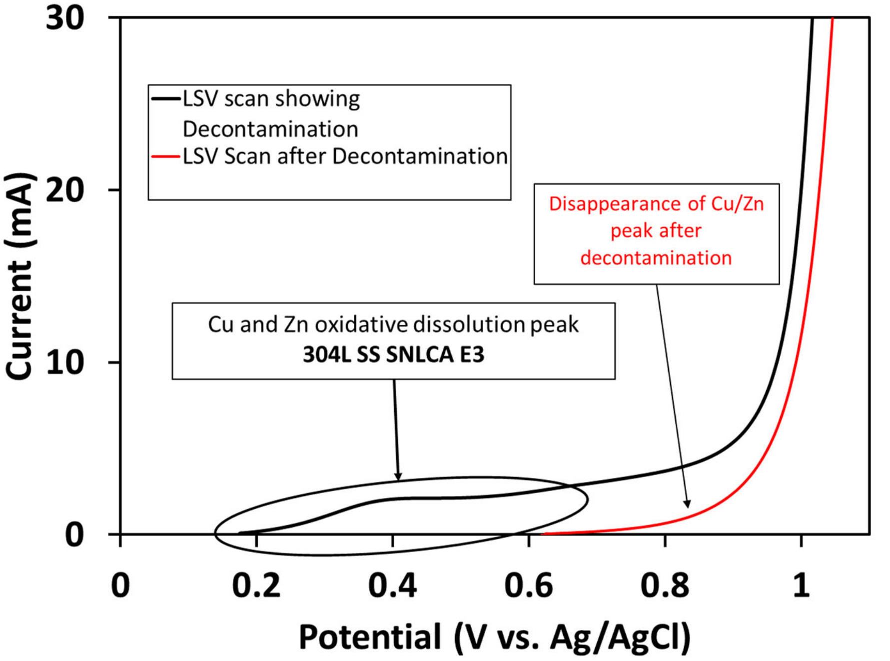


Figure 1. The LSV scans of a 304L filter sample E-3 in a 20% nitric electrochemical bath.

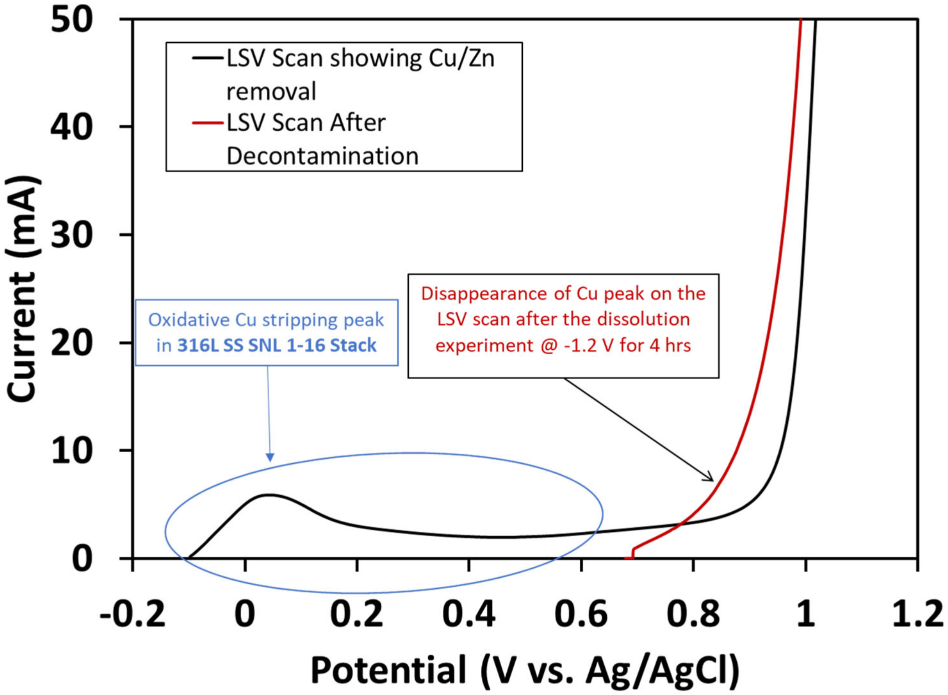


Figure 2. The LSV scans of a 316L filter sample NP201005-1-16 in a 20% nitric bath.

For the purpose of processing samples in batches, a conversion to a more conventional two-electrode setup is used for the potentiostatic experiments, wherein a fine metal lattice (unit cell is 2 mm × 2 mm × 2mm) created by metal AM is the working electrode (anode) and a platinum-coated titanium mesh is used as the counter electrode. The LSV scans of Figure 1 and Figure 2 are used to determine the dissolution potential range prior to the potentiostatic experiments, and to confirm the reduction (and/or removal) of characteristic Cu-Zn peaks after the dissolution experiments. Examples shown in Figure 1 and Figure 2 are for a 304L Sample E-3 and a 316L filter sample NP201005-1-16, respectively. Based on these results, a cell potential of -1.1 V (or greater in magnitude) is used for the electrochemical cleaning process. Time intervals of two (2) and four (4) h. are assessed for initial experiments of EDM surfaces of filters.

4. RECTANGULAR FILTER SAMPLES

4.1. 304L Filter Frames

The 304L filter samples were cleaned using an electrochemical bath of 20% HNO_3 at a 1.1V cell potential. Sample E-2 was cleaned for 2 hours, and the time was increased to 4 hours for sample E-3. The cleaned EDM-cut surface of the filter frame E-3 is shown in Figure 3 using secondary-electron (SE) and back-scattered (BS) imaging modes of the SEM. The surface contours are seen in the SE images whereas composition variations are accentuated in the BS imaging mode. The EDS measurements of composition (wt.%) from three surface areas of the cleaned EDM-cut filter frames are listed in Table 1.

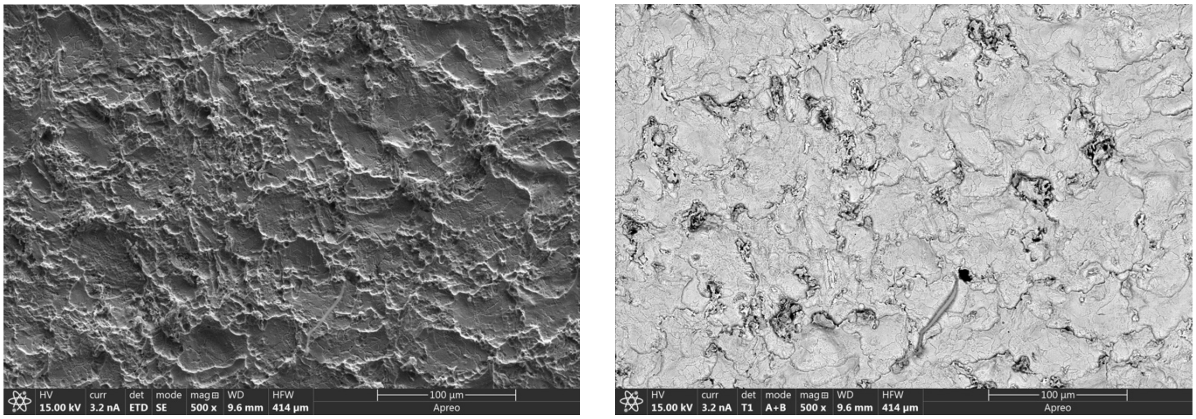


Figure 3. The center-surface of the 304L filter frame E-3 is viewed using SE (left) and BS (right) imaging modes after electrochemical cleaning for 4 h. in 20% HNO_3.

The *edge1* location is on the EDM-cut surface adjacent to one edge, and *edge2* is at the opposite side of the EDM-cut surface. The 4 h. immersion time successfully reduces the Cu-Zn contamination of the EDM-cut surface to <1 wt.%. A numerical value of zero indicated that a characteristic x-ray peak couldn't be identified in the EDS spectra, as for Zn in the cleaned condition of sample Number E-3. In further trial, samples F-1 and F-2 have shown no residual Cu-Zn recast contamination after cleaning under dissolution conditions in a 20% nitric acid bath with greater cell potentials, i.e., 1.2 V for 4 h. and 1.3 V for 3 h., respectively. Table 1 also contains the EDS measurements for these two cleaned samples, F-1 and F-2.

To reduce any adverse effects of a concentrated nitric-acid solution, a more dilute 5% bath is experimented with for samples 304L filter sample F-6. A 3 h. exposure at a higher cell potential of -1.7 V was successful to remove all residual brass contamination. An increase in the oxidative potential should speed up the rate of dissolution whereas the reduced concentration will slow corrosive attack. However, to reduce the processing time for EDM recast dissolution, a higher solution concentration of 20% nitric is maintained but at a higher cell potential. For example, complete EDM removal was observed for sample H-1 as processed at 1.4 V for 1 h. and for sample H-2 as processed at 3.2 V for 30 minutes. The EDS measurements are listed in Table 1 as well for sample H-1. However, apparent etching of the EDM-cut surface progresses as seen in Figure 4, from 1.4 V (left) to 3.2 V (right). An increase to high cell potentials leads to break down of the solution, a loss of cleaning effectiveness, and can create adverse surface finish effects.

Table 1. EDS Composition (wt. %) of 304L Filter Frame Cleaned in 20% HNO

Spectrum	Fe	Cr	Mo	Mn	Si	Ni	Cu	Zn	O	Location
E-2_1	58.7	22.6	-	2.4	0.44	7.4	4.2	0.56	3.8	*center*
E-2_1.1	62.9	19.7	-	2.3	0.44	8.8	3.6	0.70	5.5	*edge1*
E-2_2.1	60.3	21.8	-	2.3	0.46	7.8	3.8	0.37	3.3	*edge2*
E-3_5	66.7	19.7	-	2.2	0.35	9.2	0.97	0	0.88	*center*
E-3_1.6	67.0	19.5	-	2.2	0.39	9.3	0.82	0	0.82	*edge1*
E-3_2.1	67.8	19.3	-	2.1	0.38	9.5	0.35	0	0.50	*edge2*
F-1_1.1	67.6	20.1	-	2.2	0.67	8.8	0	0	0.63	*center*
F-1_1.2	67.7	21.0	-	2.2	0.60	8.7	0	0	0.62	*edge1*
F-1_1.3	67.7	20.1	-	2.2	0.65	8.7	0	0	0.56	*edge2*
F-2_1.1	67.7	20.2	-	2.3	0.66	8.6	0	0	0.64	*center*
F-2_1.2	67.5	20.2	-	2.3	0.66	8.7	0	0	0.66	*edge1*
F-2_1.3	67.5	20.3	-	2.3	0.64	8.6	0	0	0.61	*edge2*
H-1_1	68.1	20.9	-	1.9	0.61	8.5	0	0	-	*center*
ref 304L	*balance*	*18-20*	-	*2*	*0.75*	*8-12*	-	-	-	-

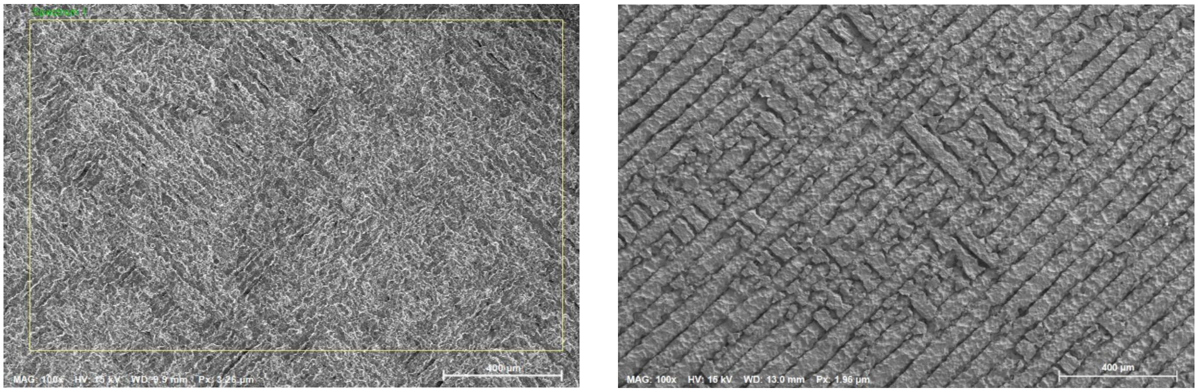


Figure 4. The EDM recast layer is fully removed but the 20% nitric bath appears to etch the sample surface as the cell potential is raised from 1 h. at -1.4 V (left) for sample H-1 to 30 min. at -3.2 V (right) for sample H-2.

4.2. 316L Filters

Images of the EDM-cut surfaces are shown in Figure 5 for 316L filter samples NP201005-1-1 and 1-7. The smooth surface of the Cu-Zn recast layer is evident clearly throughout the surface images. Figure 6 shows higher magnification images of the lattice structure within the filter. The appearance of nodular particulates, 10-30 µm in size, decorates the lattice surface.

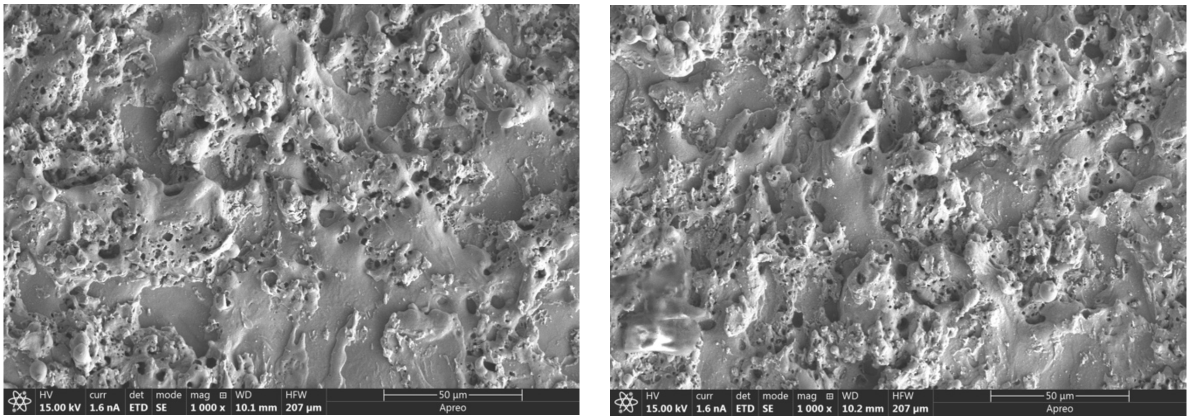


Figure 5. The center-surfaces of the 316L filter frames -1-1 (left) and -1-7 (right) are viewed using SE imaging modes before cleaning to remove the EDM recast layer.

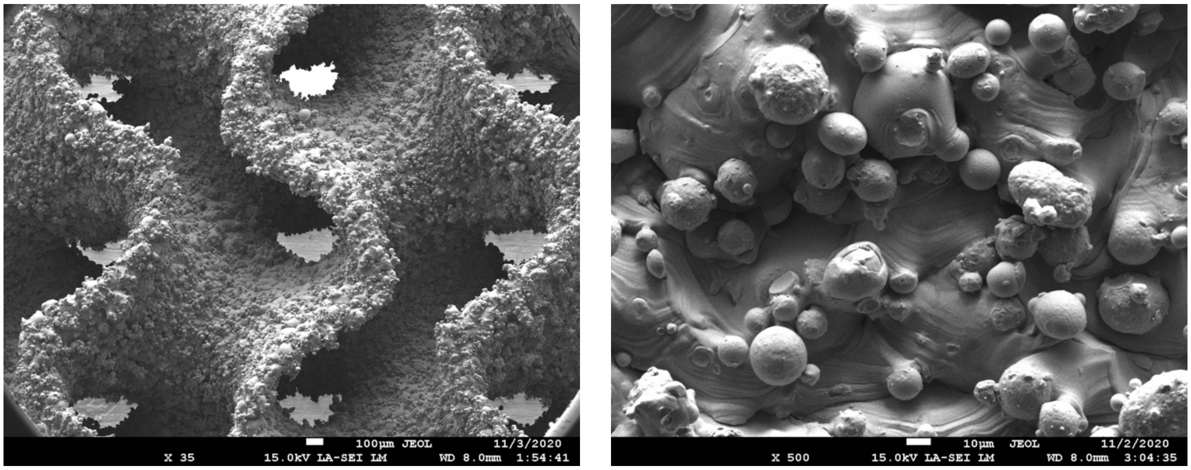


Figure 6. SEM images of the lattice structure away from the EDM cut surface for samples -1-1 (left) and -1-7 (right).

The EDS measurements of composition (wt.%) from the surfaces of samples -1-1 and -1-7 are listed in Table 2. The spectra include measurements from the center region of EDM-cut surfaces and the surface of the lattice elements within the interior of the filter support frame. Contamination at the EDM-cut surface can easily reach levels of 20 wt.% Cu. The samples are examined again after electrochemical cleaning.

Prior to the electrochemical processing, a pre-cleaning of the components was accomplished in a heated (130-135 °F) and sonicated aluminum NST detergent for 90 min. followed by a 10 min. deionized water rinse. The electrochemical baths used to dissolve the EDM recast layer are: 3% NaCl; and 20% nitric acid (as used at room temperature with a stir rate of 300 rpm). The electrochemical process utilizes three-electrode configuration consisting of an Ag/AgCl reference electrode, a platinum-coated titanium mesh (cathode), and the 316L filter component as the working (anode) electrode. The conditions of cell potential and exposure time are summarized in Table 3.

Table 2. EDS Composition (wt.%) of EDM-cut Surfaces of 316L AM Filter

Spectrum	Fe	Cr	Mo	Mn	Si	Ni	Cu	Zn	O	Location
-1-1_1	42.3	12.0	1.7	1.1	1.2	5.5	20.5	9.4	6.3	EDM-center
-1-1_3	61.3	18.8	2.2	2.8	1.5	9.6	0	0	3.8	lattice
-1-1_4	62.6	18.6	2.4	2.5	1.1	9.8	0	0	3.0	lattice
-1-7_1	40.8	11.7	1.7	1.0	1.4	5.2	20.5	11.4	6.3	EDM-center
-1-7_2	50.9	14.7	2.3	1.2	0.8	7.2	15.1	3.9	4.0	EDM-center
-1-7_3	62.6	19.1	2.0	2.5	1.2	9.6	0	0	3.0	lattice
ref 316L	*balance*	*16-18*	*2-3*	*<2*	*<0.75*	*10-14*	-	-	-	-

Table 3. Cleaning Conditions for Each 316L AM Filter Sample

Sample	-1-1	-1-7	-1-8	-1-16	-1-27	-1-33
bath solution	3% NaCl	3% NaCl	20% nitric	20% nitric	20% nitric	20% nitric
cell potential (V)	0.5	0.6	1.2	1.1	1.3	1.4; 1.3
exposure time (h)	3	5	4	4	1	0.1; 1

SEM images of sample -1-7 are shown in Figure 7 after an electrochemical cleaning for 5 h. in a 3% sodium chloride (NaCl) bath at -0.6 V cell potential. A Cu x-ray map (right) superimposed on an image (left) of the processed surface shows that a residue of Cu remains.

SEM images of sample -1-8 are shown in Figure 8 after an electrochemical cleaning for 4 h. in a 20% nitric acid (HNO_3) bath at a -1.2 V cell potential. Although a one (1) h exposure time at -1.4-2 V is now found to be sufficient for removing Cu-Zn contamination from the surface of 304L samples, longer exposure times were used to assess the effect of dissolution of EDM contamination beneath the exposed surface. Surface contours are seen in the SE images whereas composition variations are accentuated in the BS imaging mode. A cross-hatched pattern to the surface structure emerges as would be consistent with the laser raster pattern during the LPBF synthesis process. Similar results are found for fully cleaned 304L filters as samples F-1 and F-2.

The EDS measurements of composition (wt.%) from surfaces of electrochemically processed samples -1-7, -1-8, -1-16, -1-27, and -1-33 are listed in Table 1. (Dashes in Table 4 indicate that the element was not included in the normalized computation of composition.) The results for sample -1-7 are consistent with the Figure 7 x-ray map where a residue of 2 wt.% Cu remains.

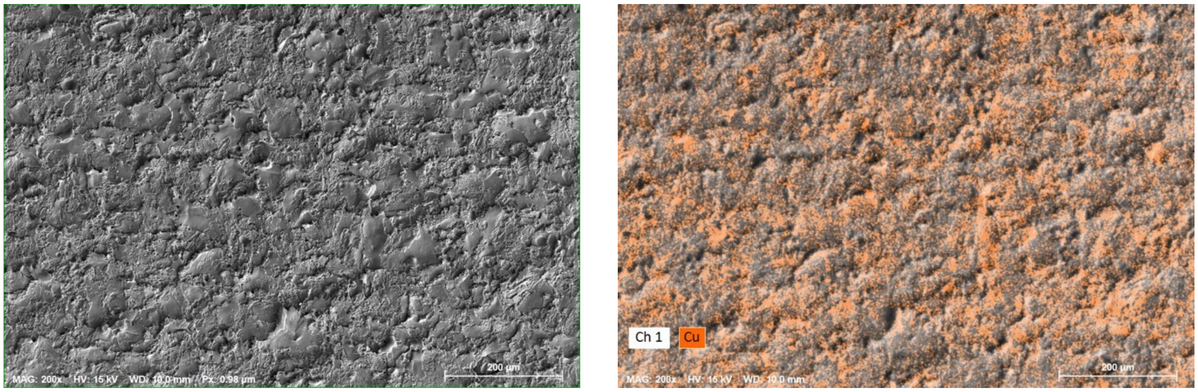


Figure 7. SEM images of sample -1-7 using SE imaging mode (left) and with a Cu x-ray map overlay after electrochemical cleaning in 3% NaCl solution.

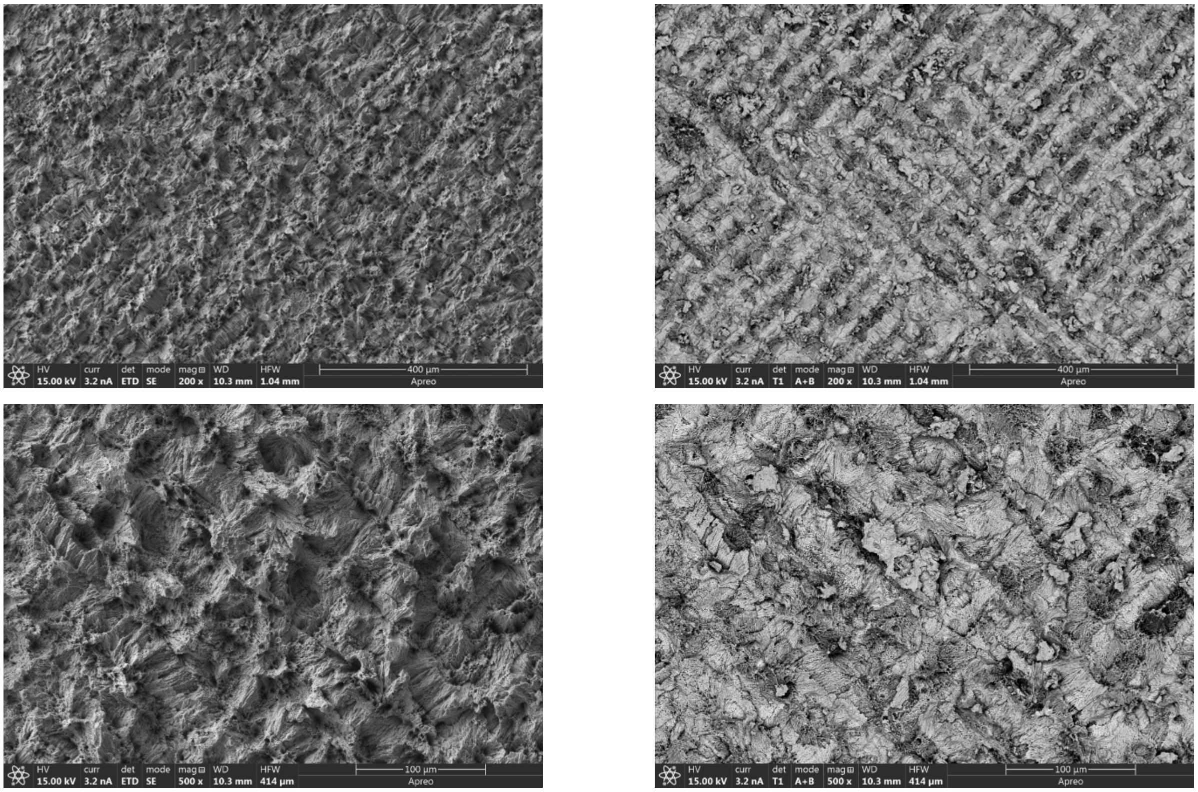


Figure 8. The surface at the center of the 316L filter frame -1-8 is viewed using SE (left) and BS (right) SEM modes after electrochemical cleaning in the 20% HNO_3 solution, where higher magnification images are seen on the bottom row of top row images

The 4 h. immersion time at a potential of -1.2 V appears to remove the Cu-Zn contamination of the EDM-cut surface from sample -1-8. The characteristic x-ray peaks for Cu at 8 keV and <1 keV, as well as Zn, couldn't be distinguished from background (with threshold values <0.5 wt.%) in the Figure 9 EDS spectra for the cleaned component -1-8.

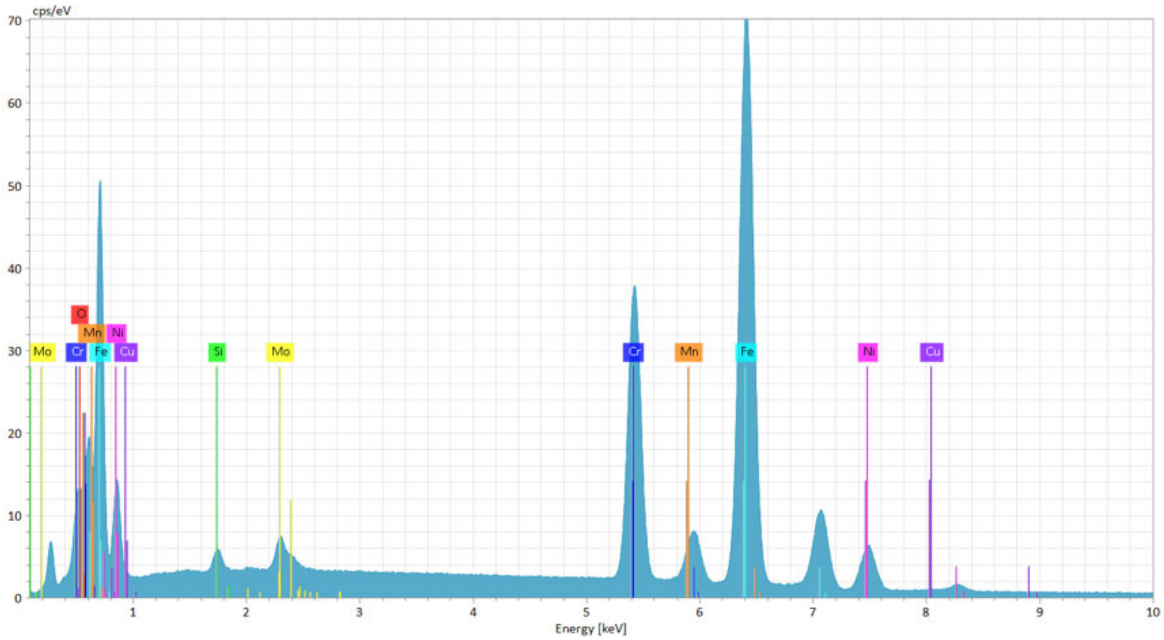


Figure 9. The EDS spectrum of 316L filter frame -1-8_c after electrochemical cleaning at -1.2 V for 4 h. in 20% HNO_3.

Table 4. EDS Composition (wt.%) of Surfaces after Electrochemical Cleaning

Spectrum	Fe	Cr	Mo	Mn	Si	Ni	Cu	Zn	O	Frame
-1-7_e1	67.6	17.3	1.0	1.8	-	9.9	2.1	0.3	-	edge1
-1-7_c	67.7	17.4	1.0	1.8	-	10.0	2.0	0.1	-	center
-1-7_e2	67.6	17.2	1.0	1.8	-	9.9	2.1	0.4	-	edge2
-1-8_e1	67.4	18.6	2.4	2.1	0.6	8.4	0	0	0.5	edge1
-1-8_c	67.4	18.6	2.4	2.1	0.7	8.3	0	0	0.5	center
-1-8_e2	67.4	18.6	2.3	2.1	0.7	8.4	0	0	0.5	edge2
-1-16_e1	65.7	17.5	2.3	1.9	0.5	9.2	1.5	0.1	1.3	edge1
-1-16_c	65.5	17.6	2.3	1.9	0.5	9.0	1.7	0.1	1.4	center
-1-16_e2	66.1	17.8	2.3	2.0	0.5	8.8	1.2	0	1.3	edge2
-1-27_e1	66.6	17.9	1.3	2.1	0.4	9.3	2.2	0.2	-	edge1
-1-27_c	66.5	17.9	1.3	2.1	0.5	9.4	2.1	0.2	-	center
-1-27_e2	67.1	18.1	1.3	2.2	0.4	9.1	1.7	0.1	-	edge2
-1-33_e1	68.5	19.4	1.0	2.0	0.3	8.1	0.7	0	-	edge1
-1-33_c	67.0	18.5	1.2	2.3	0.4	8.7	1.8	0.1	-	center
-1-33_e2	67.3	18.5	1.2	2.2	0.4	8.7	1.6	0.1	-	edge2
ref 316L	*balance*	*16-18*	*2-3*	*<2*	*<0.75*	*10-14*	-	-	-	-

The results found for samples -1-16, -1-27, and -1-33 indicate that a residue of Cu remains after cleaning. Attempts were made to reduce process times during dissolution. Success was later accomplished for samples processed using higher cell potentials.

4.3. Surface Penetration

The depth of the EDM recast contamination layer can be assessed using a cross-section of the EDM-cut surface as achieved through focused-ion-beam (FIB) milling. A Gallium (Ga) ion source is accelerated at the exposed surface to cut a small window of material that creates a cross-section view of the cleaned EDM surface. For the FIB sectioning, the sample surface is initially coated with a layer of platinum (Pt) to preserve all of the surface features by encapsulation. The window of material is lifted out of the trench after the FIB milling process and then examined using SEM methods including elemental x-ray mapping of the section and EDS composition mapping analysis. This enables a localized examination of the microstructure to determine the level of mixing between Cu-Zn and the stainless-steel surface that results from the EDM wire cutting process, including the extent to which Cu-Zn may be buried beneath the cleaned surface. As a result, this mixing can be a source of porosity at the EDM-cut surface where Cu-Zn is dissolved away.

The first result for a cleaned EDM surface of a 304L filter is shown in Figure 10. This material corresponds to that shown in Figure 3. The 10μm-thick Pt layer is readily seen above the cleaned EDM-cut surface. The x-ray maps for Cr, Mn, Pt, Cu, Zn, and O that correspond to the SEM image (left) in Figure 8 indicate a concentration, or perhaps precipitation, of Cr and Mn from the 304L alloy within the mixed zone that extends 2-to-15 μm beneath the free surface.

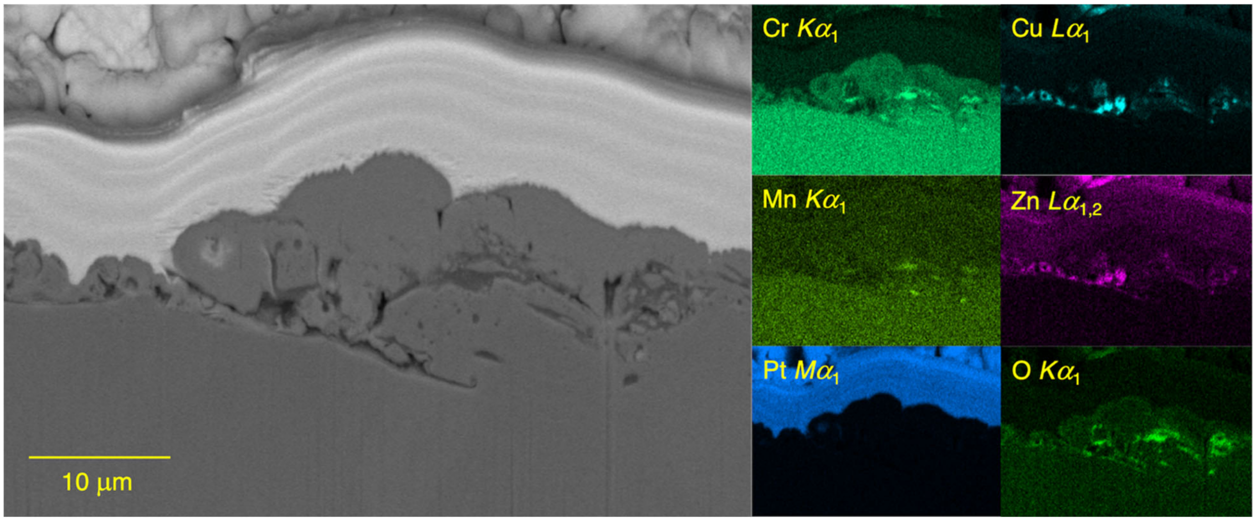


Figure 10. A FIB-SEM view of a 304L filter with x-ray maps that reveal Cu and Zn residue that remains at the electrochemically cleaned EDM-cut surface.

Locations of Cu and Zn are seen as well at the cleaned EDM-cut surface in Figure 10. If the 20% nitric solution penetrates in this buried region, as appears in this region of section depicted in Figure 10, then isolated porosity within 10 μm of the surface would result. Regions of higher O content are seen within the mixed region at the surface.

The second result is for a cleaned EDM surface of a 316L filter. A closer look at the depth of the intermixing that occurs during the EDM cutting process is seen in the FIB cross-section images of Figure 11. The Pt overcoat layer is readily seen above the cleaned EDM-cut surface. The x-ray maps for Cr, Cu, Mn, Fe, Pt, and O that correspond to the Figure 11 SEM image (left) is used to identify a concentration or perhaps precipitation of solutes from the 316L alloy within the mixed zone that extends several microns beneath the free surface. If the dissolution process penetrates into the mixed/buried region, then isolated porosity within of the near surface would result. Regions of higher O content are seen within the mixed region at the surface. A singular concentration, or perhaps precipitation, of Cr from the 316L alloy and O within the mixed zone that extends 2-to-5 μm beneath the free surface. Locations of concentrated regions of Cu (and Zn) are not seen at the cleaned EDM-cut surface as clearly defined by the Fe x-ray map interface with the Pt overcoat. However, some diffuse stringers of Cu appear within the curled region of the Fe – perhaps, buried from surface exposure. Regions of higher O content are seen within the mixed region at and within the near surface region.

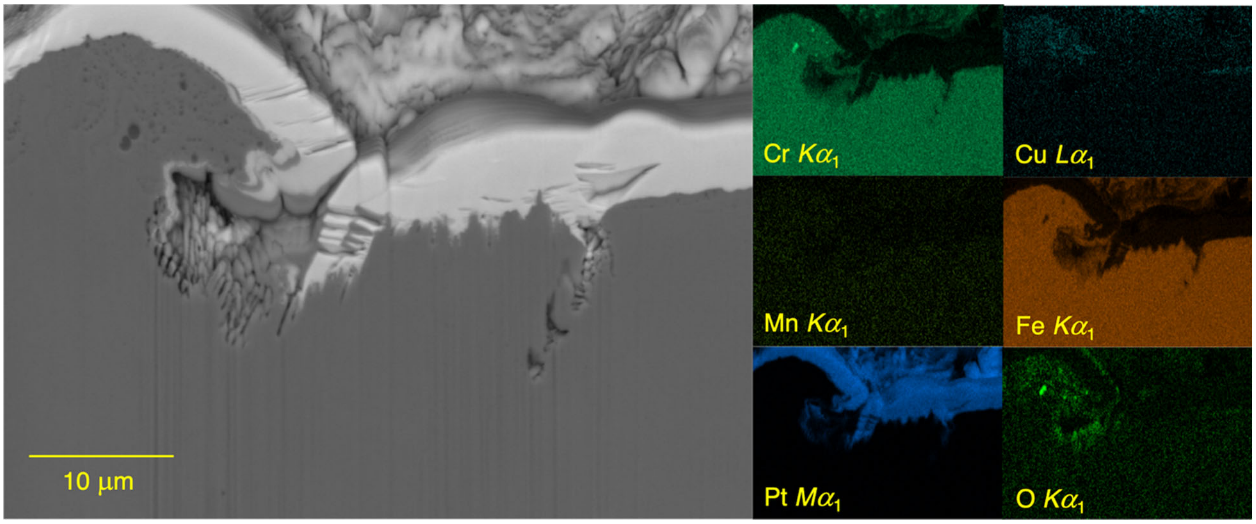


Figure 11. A FIB-SEM view of a 316L filter with x-ray maps that reveal Cu and Zn residue that remains at the electrochemically cleaned EDM-cut surface.

4.4. Abrasive Removal

As an alternate to electrochemical cleaning, surface grinding (as seen in Figure 12) was attempted to remove the EDM recast layer. EDS measurements of five locations on this sample were made on which the EDM cut surface had been ground using an abrasive media. The locations of the EDS spectrum are shown in Figure 12 with corresponding elemental composition data is listed in Table 5. The results indicate that the brass contamination has been fully removed, although the depth of the grinding process is unknown. Some residual contamination from the abrasive material appears to be present in the EDS spectra.

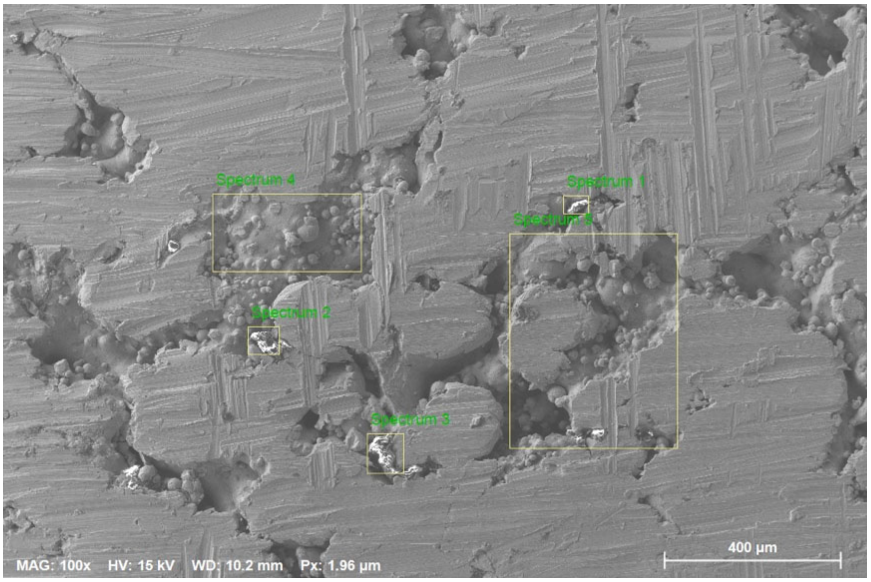


Figure 12. An SEM image of the ground filter surface to remove the EDM recast layer.

Table 5. EDS Composition (wt. %) after Grinding the EDM-cut Surface

Spectrum	Fe	Cr	Mo	Mn	Si	Ni	Cu	Zn	O	Ca	Al	C
spectrum_1	62.2	16.1	1.2	1.7	0.5	9.6	0	0	1.6	0.2	0.8	6.1
spectrum _2	57.3	17.1	1.1	3.4	0.9	8.5	0	0	3.2	0.2	0.4	7.9
spectrum _3	59.4	16.1	1.2	2.3	0.6	9.0	0	0	2.2	0.3	0.3	8.7
spectrum _4	63.7	17.5	1.3	2.5	0.7	10.0	0	0	2.0	0.3	0.5	1.6
spectrum _5	64.5	17.3	1.2	2.4	0.6	9.7	0	0	1.6	0.2	0.3	2.4
average	*61.4*	*16.8*	*1.2*	*2.4*	*0.7*	*9.3*	*0*	*0*	*2.1*	*0.2*	*0.4*	*5.4*
ref 316L	*balance*	*16-18*	*2-3*	*<2*	*<0.75*	*10-14*	*-*	*-*	*-*	*-*	*-*	*?*

5. METAL AM LATTICES

5.1. Dissolution at High Cell Potential

The application of the electrochemical dissolution process was applied to the "doorstop" prototype components to remove the EDM recast layer contamination. Samples were measured before and after cleaning. Elemental composition is measured in a scanning electron microscope (SEM) equipped with EDS that uses the intensity of characteristic x-rays to determine the near surface composition (to a typical depth up to 3 μm for <10 keV x-rays). Values for compositions are measured at point locations as indicated in Figure 13 from the base of doorstop sample 3S (G-1) and are listed in Table 6, along with measurements from samples 8H (G-2), 4S (G-5), and I-2 through I-5. The amount of Cu and Zn contamination is not uniform but varies widely from point to point as seen in the Table 6 results.

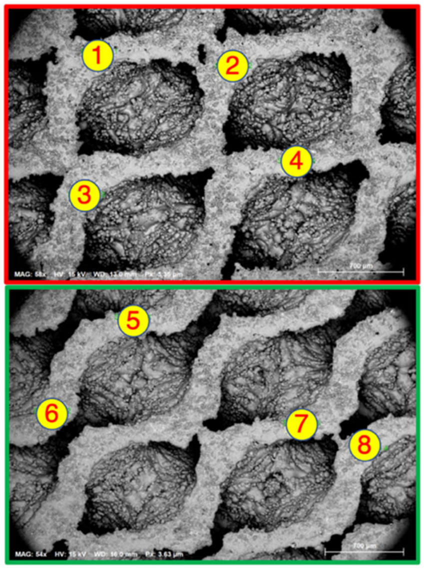


Figure 13. SEM images at top and bottom of sample 3S (G-1) before cleaning the filter.

Table 6. EDS Composition (wt. %) of Metal Lattice Base Surfaces after EDM Cutting

Spectrum	Fe	Cr	Mo	Mn	Si	Ni	Cu	Zn	O	Filter
3S(G1)_1	51.26	21.69	1.37	2.89	1.15	4.04	3.00	8.73	5.87	top
3S(G1)_2	34.74	8.90	2.38	0.97	0.44	2.90	14.74	24.57	10.35	top
3S(G1)_3	14.41	4.11	1.65	0.46	1.40	1.30	41.44	30.06	5.18	top
3S(G1)_4	55.74	15.03	2.81	1.66	0.68	6.81	0.85	7.10	9.31	top
3S(G1)_5	42.78	9.51	2.00	1.05	0.22	2.15	6.73	26.37	9.19	bottom
3S(G1)_6	29.10	5.99	3.61	0.59	0.56	2.59	20.81	22.42	14.33	bottom
3S(G1)_7	32.34	8.95	10.99	0.79	0.50	3.48	0.71	5.02	37.25	bottom
3S(G1)_8	27.26	5.44	3.68	0.54	0.79	2.32	19.10	25.66	15.20	bottom
8H(G2)_1	64.37	20.81	0.67	2.68	0.00	3.84	5.56	0.87	1.19	top
8H(G2)_2	61.22	16.85	4.64	1.66	0.42	8.26	3.17	0.39	3.40	top
8H(G2)_3	36.90	11.23	6.66	1.03	0.46	4.64	21.75	6.13	11.20	top
8H(G2)_4	56.56	15.44	6.37	1.51	0.63	7.68	6.97	0.54	4.32	top
8H(G2)_5	56.73	16.46	5.68	1.36	0.67	7.90	2.85	1.78	5.73	bottom
8H(G2)_6	60.16	16.96	6.13	1.39	0.68	8.50	1.08	0.84	4.24	bottom
8H(G2)_7	55.93	16.28	5.29	1.38	0.82	7.68	2.74	2.73	7.14	bottom
8H(G2)_8	59.21	16.95	7.75	1.71	0.56	8.63	0.92	0.94	3.33	bottom
4S(G5)_1	52.35	16.34	-	1.68	1.35	5.87	10.21	12.21	-	top
4S(G5)_1	49.66	12.19	-	1.29	1.12	4.14	8.69	22.92	-	bottom
ref 304L	*balance*	*18-20*	-	*<2*	*<0.75*	*8-12*	-	-	-	-

These doorstop samples are next cleaned according to the conditions of cell potential and exposure time as listed in Table 7. Prior to the electrochemical dissolution in nitric acid, a heated and sonicated (4% by vol.) aluminum NST detergent treatment is followed by a 10 min. deionized water rinse.

Table 7. Cleaning Conditions for Each 316L AM Filter Sample

Sample	3S (G-1)	8H (G-2)	4S (G-5)	G-14	G-15	G-16	I-2-to-5
NST bath (°F)	135	135	135	135	200	200	150
NST exposure (h)	1.5	1.5	1.5	1.5	0.5	0.75	1
nitric bath conc (%)	5	5	20	20	20	20	20
cell potential (V)	1.7	1.8	2.5	2.0	2.0	2.0	2.0
nitric exposure (h)	3	3	0.5	0.75	0.75	0.75	1

Experiments were again conducted with LSV at a 10 mV·s^{-1} scan rate to confirm the presence and removal of Cu at the EDM-cut surface. The electrochemical process utilizes three-electrode configuration consisting of a Ag/AgCl reference electrode, a Pt sheet cathode, and the 304L metal

AM lattice component as the working (anode) electrode. A final rinse of the component to remove chemical contamination consisted of deionized (DI) water with sonication for 10 min. The results of the EDS measurements from spectrum collected over the entire area depicted at the top and bottom locations within the filter as shown in Figure 13 are listed in Table 8.

Images of the cleaned surfaces from the top of sample 8H (G-2) are shown in Figure 14 as taken from the frame (left) and filter (right). It is noted that pinhole regions appear in the surface of the frame after cleaning as a result of the dissolution of Cu-Zn embedded below the surface of the EDM recast layer as previously seen in Figure 10.

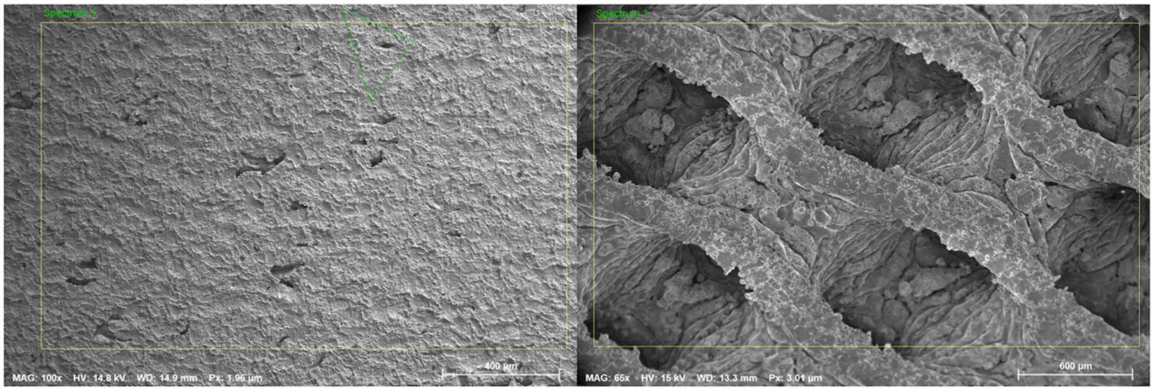


Figure 14. SEM images at top of sample no. 8H (G-2) from the frame (left) and filter (right) after cleaning.

A more aggressive condition for electrochemical dissolution results for the higher nitric concentration and higher potential used for sample I-2 as listed in Table 8 and shown in Figure 15 where the laser raster pattern during the build is revealed from selective etching of grain boundaries within the solidification structure.

Table 8. EDS Composition (wt. %) of Metal AM Lattice Surfaces after EDM Cleaning

Spectrum	Fe	Cr	Mo	Mn	Si	Ni	Cu	Zn	O	Filter
3S(G1)_1	67.08	20.41	-	2.59	0.69	8.90	0.30	0.02	-	top
3S(G1)_2	67.06	20.38	-	2.56	0.64	8.92	0.43	0.01	-	bottom
8H(G2)_1	67.76	20.76	-	1.82	0.71	8.83	0.12	0.00	-	top
8H(G2)_2	67.58	21.07	-	1.67	0.62	8.92	0.14	0.00	-	bottom
4S(G5)_1	66.09	21.55	-	1.84	0.84	8.47	1.10	0.12	-	top
4S(G5)_1	65.96	21.31	-	1.78	1.01	8.50	1.23	0.21	-	bottom
G-14_1	67.00	21.18	-	1.87	0.89	8.66	0.40	0.00	-	top
G-14_2	66.86	21.41	-	1.87	0.81	8.58	0.48	0.00	-	bottom
G-15_1	67.86	20.73	-	1.54	0.54	8.59	0.19	0.00	-	top
G-15_2	67.69	20.74	-	1.62	0.61	8.89	0.45	0.00	-	bottom

Spectrum	Fe	Cr	Mo	Mn	Si	Ni	Cu	Zn	O	Filter
G-16_1	67.43	21.11	-	1.47	0.57	8.53	0.23	0.00	-	top
G-16_2	67.50	21.13	-	1.50	0.63	8.95	0.29	0.00	-	bottom
I-2_1	68.13	20.67	-	1.91	0.65	8.64	0.00	0.00	-	top
I-2_1	68.17	20.46	-	1.80	0.66	8.91	0.00	0.00	-	bottom
I-3_1	67.94	20.96	-	1.99	0.64	8.47	0.00	0.00	-	top
I-3_1	68.25	20.39	-	1.83	0.64	8.89	0.00	0.00	-	bottom
I-4_1	67.83	21.14	-	1.97	0.65	8.41	0.00	0.00	-	top
I-4_1	68.36	20.15	-	1.73	0.64	9.12	0.00	0.00	-	bottom
I-5_1	68.06	20.76	-	1.82	0.60	8.76	0.00	0.00	-	top
I-5_1	68.15	20.55	-	1.80	0.63	8.87	0.00	0.00	-	bottom
ref 304L	*balance*	*18-20*	-	*<2*	*<0.75*	*8-12*	-	-	-	-

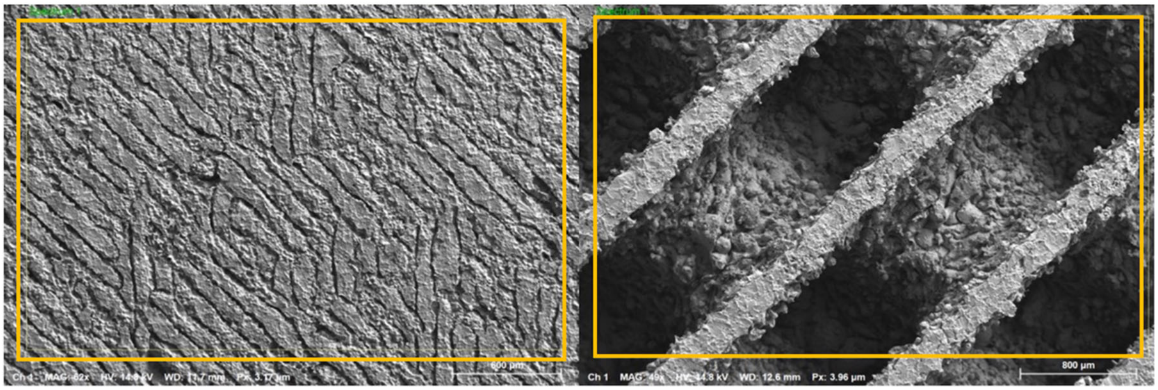


Figure 15. SEM images at top of sample I-2 from the frame (left) and filter (right) after cleaning.

In addition, area scans are taken from the frame of sample 8H (G-2) adjacent to the top and bottom regions of the filter. Cu compositions of 0.79 and 0.39 wt.% with Zn compositions of 0.03 and 0.00 wt.% are measured from these top and bottom frame areas, respectively. In comparison, area scans are taken from the frame of sample 4S (G-5) adjacent to the top and bottom regions of the filter. Cu compositions of 3.23 and 3.50 wt.% with Zn compositions of 0.37 and 0.35 wt.% are measured from these top and bottom frame areas, respectively, indicating that the 4S (G-5) sample electrochemical-cleaning conditions were not as nearly effective as those for sample 8H (G-2). Data is listed in Table 8 for EDS area spectra taken as well from cleaned samples G-5, G-14-to-16, and I-2-to-5. After cleaning, residual contamination values for Cu are all consistently less than 0.50 wt.% (a nominal Cu contamination in the source 340L powders) excluding the data for sample 4S (G-5). The I-lot samples show apparent complete removal of both Cu and Zn contamination after a 1 h exposure at a -2 V potential. It should be noted that the absolute values of EDS measurements of Cu below 0.1 wt.% become accurate due to signal-to-noise resolution. Wavelength dispersive spectrometry or mass spectroscopy analysis should be used for that purpose. The results of composition measurements are consistent with the changes observed in the LSV scans of sample 3S

(G-1), as shown in Figure 16, before and after the electrochemical dissolution process that indicate the surface contamination has been removed.

The effectiveness of the electrochemical dissolution treatment is next evaluated by sectioning the component, i.e., to provide an x-axis view of the y-z plane of the build direction. An example is shown in Figure 17 for sample 3S (G-1). EDS data is collected from areas within the surfaces of the filter interior, but not the planarized surface cut to reveal the interior. The data for the sectioned, sample 3S (G-1) cleaned in a 5% nitric solution for 180 min. is listed in Table 9 for the interior surface regions of Figure 17.

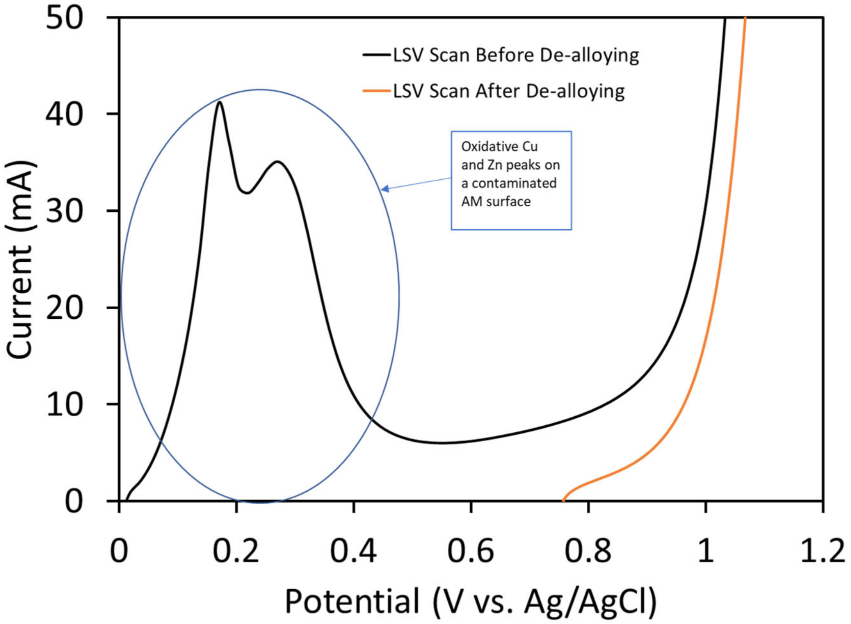


Figure 16. The LSV scans of sample 3S (G-1) before and after electrochemical dissolution of the EDM recast layer.

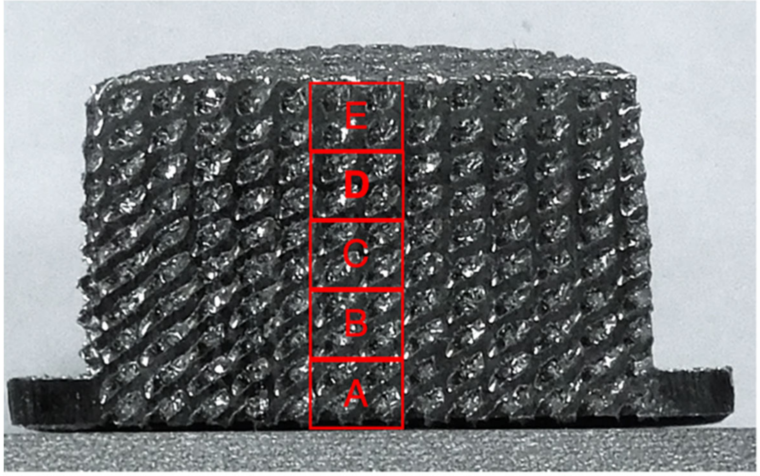


Figure 17. The cleaned sample 3S (G-1) is sectioned for the measurement of interior filter surfaces.

Table 9. EDS Composition (wt. %) of Interior Filter Surfaces after Cleaning

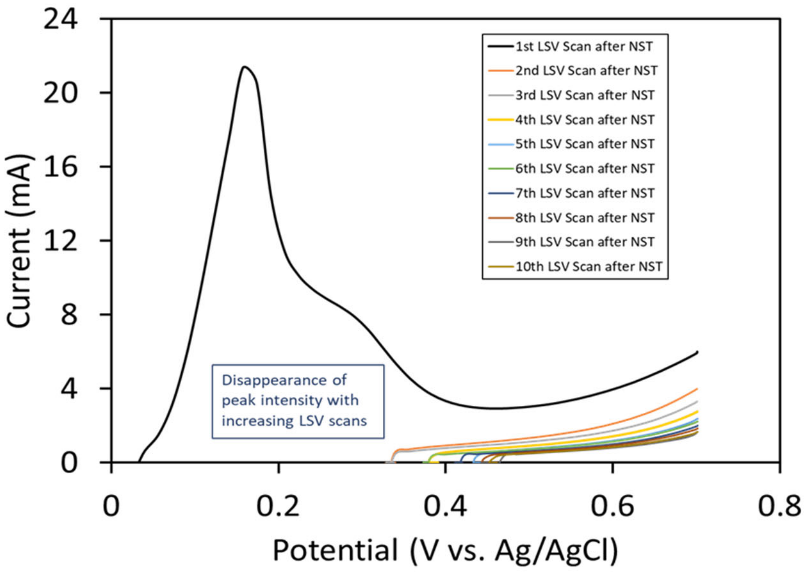
Spectrum	Fe	Cr	Mo	Mn	Si	Ni	Cu	Zn	O	Region
3S(G1)_2	67.40	20.50	-	1.71	0.74	8.79	0.87	0.00	-	A
3S(G1)_4	67.60	20.28	-	1.55	0.74	9.43	0.30	0.10	-	A
3S(G1)_3	66.74	20.49	-	1.86	1.18	9.34	0.24	0.15	-	B
3S(G1)_4	67.31	20.21	-	1.62	0.89	9.65	0.28	0.04	-	B
3S(G1)_2	66.63	20.41	-	1.62	1.42	9.56	0.26	0.10	-	C
3S(G1)_3	67.28	20.45	-	1.87	0.87	9.33	0.19	0.00	-	C
3S(G1)_3	67.46	19.94	-	1.62	0.77	9.94	0.43	0.00	-	D
3S(G1)_4	67.33	20.40	-	1.55	0.80	9.78	0.31	0.00	-	D
3S(G1)_3	67.23	20.31	-	1.55	0.74	9.77	0.33	0.06	-	E
3S(G1)_4	67.35	19.91	-	1.37	1.08	9.75	0.54	0.00	-	E
I-2_2	68.38	19.73	-	1.75	0.64	9.42	0.07	0.00	-	A
I-2_3	68.18	19.93	-	1.76	0.66	9.36	0.12	0.00	-	A
I-3_1	68.18	20.02	-	1.78	0.68	9.27	0.07	0.00	-	A
I-3_2	67.20	22.43	-	2.12	0.60	8.71	0.05	0.02	-	A
I-4_1	67.72	21.22	-	1.60	0.66	8.79	0.00	0.00	-	A
I-4_2	68.40	19.78	-	1.63	0.65	9.54	0.01	0.01	-	A
I-5_1a	67.39	21.92	-	1.58	0.60	8.51	0.00	0.00	-	A
I-5_1b	67.12	21.64	-	1.50	0.64	9.07	0.04	0.00	-	A
ref 304L	*balance*	*18-20*	-	*<2*	*<0.75*	*8-12*	-	-	-	-

5.2. Dissolution at Low Cell Potential

The removal of the EDM contaminants at the aggressive conditions of high cell potentials does produce surface etching, i.e., the dissolution of the doorstop bulk. To further examine this effect, a measure of the component weight is made through the cleaning steps. To minimize the effect of lattice dissolution, a variation in the concentration of the nitric acid solution is made, along with a progressive reduction in the cell potential that drive the dissolution process. A step-by-step review of the EDM cleaning process steps is first provided as follows.

Step 1 – measure the weight for each as-received specimen
Step 2 – immerse in a heated (135°F) NST cleaner bath with sonication for 90 minutes
Step 3 – rinse in ambient deionized water with sonication for 15 minutes
Step 4 – dry with nitrogen gas, and leave overnight in an air-circulated clean hood
Step 5 – measure weight to determine the amounts of contaminants, primarily the powder particulates that remain after the AM build, which are removed by NST cleaning
Step 6 – electrochemically clean at the selected cell potential and time in the selected-concentration of the circulated nitric-acid baths
Step 7 – (repeat steps 3 and 4)
Step 8 – measure weight to determine the amounts of contaminants, primarily EDM residue and etched surface material, that are removed after electrochemical cleaning

The effectiveness of these cleaning steps is seen in LSV scans of Figure 16 where oxidative peaks are electrochemically removed in the 5% nitric acid bath. To confirm dissolution of the EDM residue from the doorstop surface, LSV scans are conducted after 10 successive cycles of the (above) cleaning-step sequence show. The disappearance of the oxidative peaks in Figure 18 and the positive potential shifts during subsequent scans confirm the effectiveness of the electrochemical process to drastically reduce and remove the EDM contaminants from the lattice samples using a 10% nitric solution.



Disappearance of peak intensity with increasing LSV scans

Figure 18. The LSV scans after 10 cycles of the electrochemical dissolution process using 10% nitric acid bath.

The use of 10% and 20% nitric solutions is pursued at cell potentials less than 1.0V to assess the effectiveness in removal of EDM contaminants with minimal dissolution of the doorstop bulk. Table 10 lists the doorstop component mass after each step of the cleaning process. Values are listed for the nitric concentration (vol.%), the cell potential U (V), the electrochemical dissolution time t (min), the initial mass m_o, the mass loss cleaning Δm_{nst} after NST, the additional mass loss Δm_{nitric} after nitric acid dissolution, and the surface Cu and Zn concentration measurements c_{Cu} and c_{Zn}, respectively. The effect of the electrochemical cleaning is seen in the reduction in Cu and Zn contamination on the lattice surfaces measured at the base of the component in comparison to just the NST cleaning step for sample K3. The mass loss from nitric acid cleaning increases with increasing cell potential, exposure time, and nitric concentration.

Table 10. Loss of Doorstop Weight through Cleaning Steps

Sample	c_{nitric} (%)	U (V)	t (min)	m_o (g)	Dm_{nst} (g)	Dm_{nitric} (g)	c_{Cu} (wt.%)	c_{Zn} (wt.%)
K3	-	-	-	29.809	0.340	-	2.01	0.41
K4	-	-	-	29.916	0.275	-	-	-
K2	10	0.60	240	-	-	0.071	2.11	0.54
K5	10	0.70	240	29.502	0.186	0.116	1.31	0.24
K6	10	0.80	240	29.628	0.352	0.162	0.75	0
K7	10	0.90	240	30.186	0.128	0.277	1.1	0.20
035_5	20	0.50	600			0.011	0.90	0.20
035_6	20	0.50	1200			0.010	1.20	0.30
035_4	20	0.55	480			0.070	1.00	0.10
K11	20	0.60	240	30.070	0.209	0.286	0.91	0.13
035_3	20	0.60	420			0.198	0.60	0.20
M2	20	0.60	1440			0.243	1.00	0.20
M3	20	0.65	1440			0.458	0.90	0.10
K12	20	0.70	240	30.227	0.192	0.608	0.51	0.07
K14	20	0.70	300	29.750	0.223	0.782	0.15	0
M4	20	-0.70	1440			0.724	0.50	0.20
M5	20	0.75	1440			1.014	0	0
K10	20	0.80	180	29.957	0.324	0.692	0.37	0.02
035_2	20	0.80	180			0.371	0.50	0.10
K13	20	0.80	240	30.069	0.103	1.113	0.07	0
M6	20	0.80	300			0.265	0.90	0.10
K3	20	0.90	120	29.809	0.340	0.673	0.33	0
035_1	20	0.90	120			0.322	0.50	0
K15	20	0.90	180	29.695	0.285	1.608	0	0

While exposed to 20% nitric for 240 min, samples K11, K12, and K13 show the progressive effect of increasing cell potential from 0.6 to 0.7 to 0.8 on a concurrent increase in mass loss from 0.286 to 0.608 to 1.113 g along with a concurrent decrease in residual Cu contamination from 0.91 to 0.51 to 0.07 wt.%, respectively. Samples as M5 and K13 appear without surface contamination provided a mass loss of 1 g occurs from the electro-dissolution process. The effect of the longer 1440 minute exposure times listed in Table 10 is seen in the Figure 19 plots for the increase in mass loss and the commensurate reduction in Cu and Zn contamination.

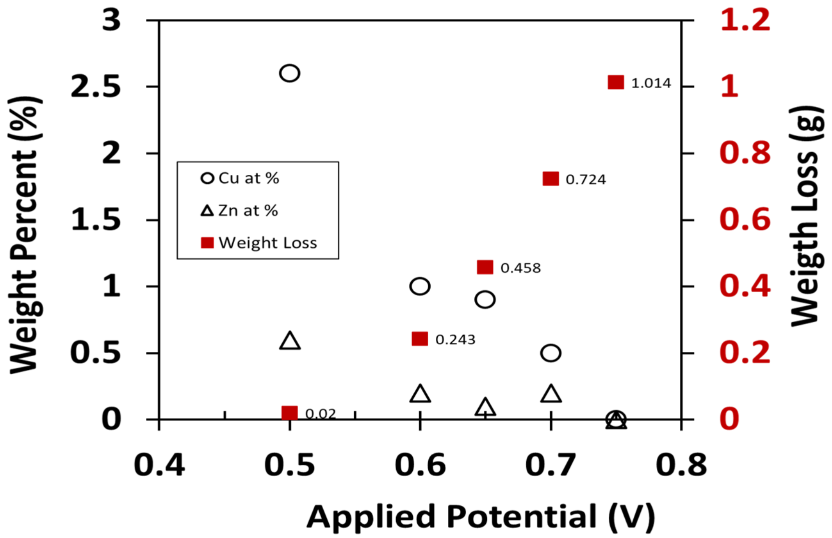


Figure 19. Mass Loss increases with a commensurate reduction in Cu and Zn contamination for 1440 min exposures in an electrochemical bath of 20% nitric acid at cell potentials less than 0.8 V.

6. SUMMARY

The EDM process produces a mixed region in locations at the wire cut surface that can trap some Cu and Zn residue within isolated areas up to 10 μm from the free surface. The contamination from the EDM recast layer varies across the EDM cut surface and is found in the through thickness of the interior filter surfaces of the 304L metal AM lattice component. The use of an electrochemical dissolution process following detergent sonication is shown to be feasible to remove the recast layer contamination from the surfaces of EDM-cut components as well as the filter surfaces in the interior of the structure. The solution chemistry, cell potential, and exposure time are all relevant variables. Optimization of the electrode geometry should be made for each electrochemical dissolution process. The key result from surface analysis using EDS indicates that an electrochemical dissolution of the Cu-Zn EDM react layer is achievable using a solution bath of nitric acid (HNO_3) with cell potentials and exposure times that are concentration dependent; for example, dissolution of the recast is accomplished at lower voltages and longer times in concentrated solution as 1.2 V for 4 h with 20% nitric from Table 3 and Table 4. Also, it is possible to remove the EDM recast at higher voltages and shorter times in more dilute solutions as at 2 V for 1 h with 20% nitric or, for a reduced attack of the host structure, at -1.8 V for 3 h. with 5% nitric a from Table 7 and Table 8. For tests conducted to account for mass loss from the cleaning steps, cell potentials greater than 0.60 V are needed to reduce the surface contamination below 1 wt.% as evidenced by the electrochemical dissolution experiments at longer exposure-times, although mass loss is minimized for potentials below this value. A compromise on dissolution of the embedded Cu and Zn contamination (as seen in Figure 11) must be made with respect to concurrent mass loss from electrochemical dissolution. The nitric acid bath was developed since it's nominally compatible with the host 304L and 316L alloys of the filters. In addition, mechanical grinding can be used to remove the recast layer but appears to leave a residue of the abrasive material in the surface. The results of the EDS composition analysis are consistent with the nominal values for the elemental composition of 316L filter. In general, slightly lower nickel and higher chromium concentrations are measured for all filter samples.

REFERENCES

[1] Technical Advance (TA): SD# 15808 Removal of Electro-Discharge-Machining (EDM) Contamination (21-05-11) A. Jankowski, B. Banga, J. Yee.

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