

Feasibility Study to Dissolve Additively Manufactured Inconel 718 Support Structures

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Additive manufacture (AM) component design face constrains due to support structure removal. Interior passages or delicate geometries require supports yet cannot be removed without compromising the design or complicating post-processing. A process was developed to dissolve metal AM supports where a sensitizing agent is applied post-build. During stress relief the sensitizing agent diffuses into the surface and alters the chemical composition of the top 100 to 200 μm . During an electrochemical dissolution process the sensitized region is susceptible to corrosion/dissolution and the etching reaction self-terminates once the sensitized region is dissolved. Support thickness varies from 80 to 200 μm , resulting in total dissolution or sufficiently weakened to facilitate removal. The objective of this project was to demonstrate a support structure dissolution process for IN718 components built using AM and to characterize the impact on mechanical properties, microstructure, and surface finish.

I. Nomenclature

<i>AM</i>	=	additive manufacture
<i>AMDE</i>	=	additive manufacture demonstration engine
<i>CSM</i>	=	Colorado School of Mines
<i>DI</i>	=	deionized
<i>E</i>	=	elastic modulus
<i>EDM</i>	=	electro discharge machining
<i>EDS</i>	=	energy dispersive spectroscopy
<i>GPa</i>	=	giga-Pascal
<i>HCF</i>	=	high cycle fatigue
<i>HIP</i>	=	hot isostatic press
IN718	=	Inconel 718
<i>L-PBF</i>	=	laser powder bed fusion
<i>mA</i>	=	milliamp
<i>mm</i>	=	millimeter
<i>MPa</i>	=	mega-Pascal
<i>MSFC</i>	=	Marshall Space Flight Center
<i>OTP</i>	=	oxygen turbo pump

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PSD	= particle size distribution
Sa	= surface roughness (arithmetic mean)
SR	= stress relief heat treatment
SEM	= scanning electron microscopy
UTS	= ultimate tensile strength
V_{SHE}	= voltage standard hydrogen electrode
XRD	= x-ray diffraction
YS	= yield strength
Z	= build direction
ϵ	= strain at failure
μm	= micrometer
$wt\%$	= weight percent
$\varnothing$	= diameter
$\%TD$	= percent theoretical density

II. Introduction

In some polymer-based Additive manufacture (AM) one polymer is used to print the part while another is used to print supports. Post-build the part is immersed in an agitated heated solution of water and ethanol to dissolve away the support structure. The support dissolution approach allows for increased design flexibility and decreases the cost of post-processing. Laser powder bed fusion (L-PBF) AM on the other hand uses the same powder feedstock to print both the part and the support structures, meaning a method to etch away supports will also etch the part, and have a direct impact on geometric dimensional accuracy, tolerance, and mechanical properties. In addition, AM component designs are constrained when using supports in that they be accessible for mechanical removal. Components with complex interior geometries requiring support structures, such as cooling channels, manifolds, and reservoirs or delicate geometries such as aerodynamic blades cannot be readily produced without either compromising design intent or greatly complicating post-processing. Therefore, a process was developed to dissolve metal AM support structures [1]. First, a sensitizing agent, such as sodium hexacyanoferrate in the case of ferrous or nickel super alloys, is applied through either full immersion or with brushes prior to heat treatment in order to relieve residual stress and obtain the desired microstructure. During heat treatment the sensitizing agent diffuses into the part and alters the chemical composition of the top 100 to 200 μm of the part's surface. For sodium hexacyanoferrate, the sensitizing agent decomposes and leaves behind a layer of carbon that diffuses into the component and decreases the corrosion resistance of this surface region by capturing the passivating elements in carbide precipitates. This effectively changes in the composition of the surface and creates a "sensitized" region that is highly susceptible to dissolution. This sensitized region is then selectively etched under conditions that preferentially dissolve the sensitized material while leaving the underlying component material unaltered. The net result is a self-terminating etch process that is geometrically agnostic, doesn't depend on electrode shape, can improve surface finish, and dissolve supports for both interior and exterior features [2]. Supports structures are single line scans, meaning that the thickness is dependent on the L-PBF machine nominal laser focus diameter and resulting melt pool, which are material and parameter specific. Support structure thickness generally vary from 80 to 200 μm , meaning that if 100 μm of material is etched, the supports will be either fully dissolved or sufficiently weak for grit blast removal [2]. Previous work completed on AM 316L stainless steel also demonstrated improved surface roughness from an R_a of 16 μm to 4 μm [1].



Fig. 1 AM metal support structure dissolution process flow shown here for 316L stainless steel [1].

III. Methodology

The objective of this project was to demonstrate a self-terminating support dissolution process for IN718 components built using L-PBF. Various sensitization and dissolution conditions were tested as well as process optimization to identify aspects that can negatively impact process consistency, such as contamination. The impact of the support structure dissolution process on mechanical properties, microstructure, and surface finish are also evaluated. Results are used to demonstrate viability to dissolve AM IN718 support structures and to determine if and how sensitization and etch process parameters can be optimized to integrate the process into existing production flows.

A. Etch Process Development

AM IN718 etch calibration disks Ø16 mm x 5 mm tall were printed on an EOS M290 at NASA Marshall Space Flight Center (MSFC) as shown in Figure 2A. Specimens were removed from the build plate without stress relief (SR) heat treatment via wire-EDM then shipped to Colorado School of Mines (CSM) for etch process development. Specimens were submerged in a saturated aqueous sodium hexacyanoferrate solution slurry at a ratio of 3.3:1 by mass of $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$ (99%) and deionized (DI) water. In order to obtain an acceptable coating specimens were submerged in slurry for 20 minutes. Specimens were then wrapped in 309 stainless steel and packed with additional slurry. Wrapped specimens underwent sensitization heat treatment at 750 °C in a nitrogen atmosphere for 24 hours in order to capture free chromium then water quenched. Specimens were then ultrasonically cleaned serially in DI water, methanol, acetone, isopropyl alcohol for 10 minutes each. An electrolytic solution was prepared of HNO_3 (0.48 M, 70 wt%) and KCl (0.1M, 99 wt%) in DI water. The etch apparatus consist of the IN718 electrode and a graphite counter electrode. Specimens were electrochemically etched for 16 hours and again ultrasonically cleaned [3].

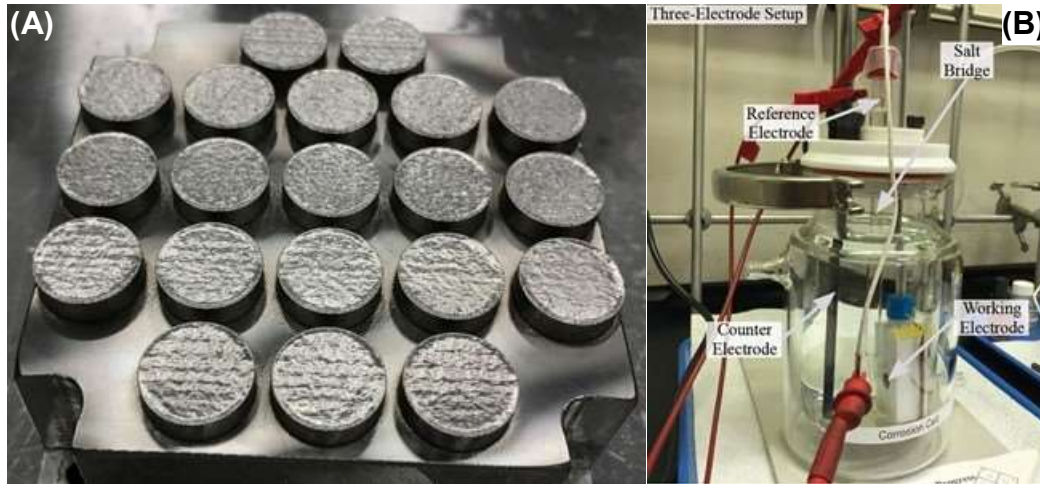


Fig. 2 AM IN718 etch calibration disks (A) and etch apparatus (B) [3].

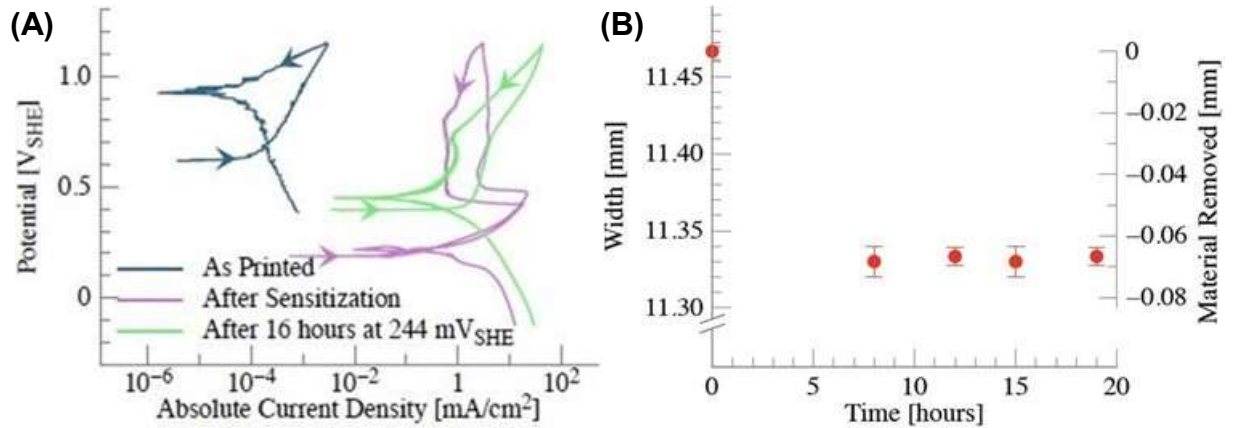


Fig. 3 IN718 post-sensitization potentiodynamic polarization plot (A). Change in specimen diameter with dissolution showing self-terminating reaction once sensitized region is dissolved (B) [3].

B. Mechanical Property Evaluation

Three IN718 concept feasibility tensile bars were printed in the vertical direction and three at a 45° angle from build direction (Z) with perforated supports on the MSFC EOS M290 as shown in Figure 4A. The tensile bars in the as-built condition with supports still attached to the build plate were shipped to CSM where they underwent the sensitization and etch. The sensitization heat treatment (750 °C for 24 hours) temperature was selected to be similar to but below the stress relief heat treatment (1065 °C for 1.5 hours) for IN718, with the exception of the longer treatment time. Specimens were then returned to MSFC for hot isostatic press (HIP), solutionize and age heat treatment per AMS 5664 as shown in Figure 4B. Tensile specimens then had threads machined in followed by tensile testing. Previous sensitization and etch efforts for 316L found that HIP before sensitization improves the etch process by consolidation of the support structures and residual powder, which was replicated for IN718 [2].

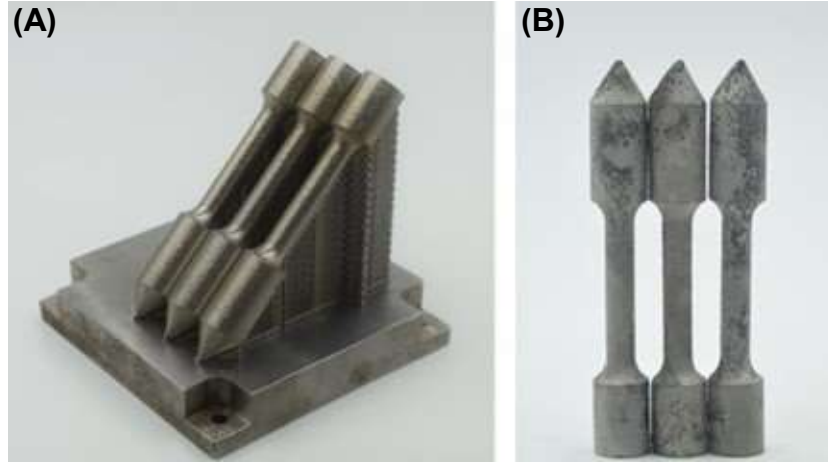


Fig. 4 AM IN718 concept feasibility tensile specimens as built (A) and post-etch (B).

The concept feasibility specimens underwent tensile testing at MSFC in according to ASTM E8 “Standard Test Methods for Tension Testing of Metallic Materials” with corresponding results compared to control AM IN718 data as shown in Table 1. It was determined that the dissolution process did not have a negative impact on yield stress (YS), ultimate tensile strength (UTS), elastic modulus (E), or strain at failure (ϵ). As expected, specimen build orientation has the dominant impact on tensile mechanical properties.

Table 1: AM IN718 concept feasibility median mechanical property comparison.

Specimen	Condition	Orientation	YS _{med} (MPa)	UTS _{med} (MPa)	E _{med} (%)	E _{med} (GPa)
Reference-Z	Control	Vertical	1154.73 ± 3.38	1379.3 ± 1.17	24.23 ± 0.27	184.37 ± 5.52
Tensile-Z	Control	Vertical	1144.53 ± 8.69	1377.43 ± 7.20	23.32 ± 0.84	193.88 ± 6.67
Tensile-45°	Etch	45°	1176.38 ± 15.45	1412.12 ± 6.75	19.68 ± 0.64	222.01 ± 2.02

Results from the concept feasibility specimen evaluation proved promising; therefore, a more thorough design of experiments was developed in order to better characterize the impact of the sensitization and etch process on AM IN718. A build layout with a larger array of specimens to include metallographic, tensile, high cycle fatigue (HCF), and surface finish specimens were printed from IN718 on the EOS M290 at MSFC as shown in Figure 5A. The build consisted of two sets of specimens printed on the same build plate and designed to be removed by hand in order to retain the support structures attached to the specimens in order for subsequent sensitization and etch process optimization as shown in Figures 5B and 5C. The control specimens had support structures mechanically removed then underwent standard heat treatment, machining, and mechanical testing. The second set of specimens with supports attached were shipped to CSM with to undergo the etch process then returned to MSFC for heat treatment, machining, and mechanical testing. Control and etch specimens underwent room temperature tensile and HCF testing under the same load conditions.

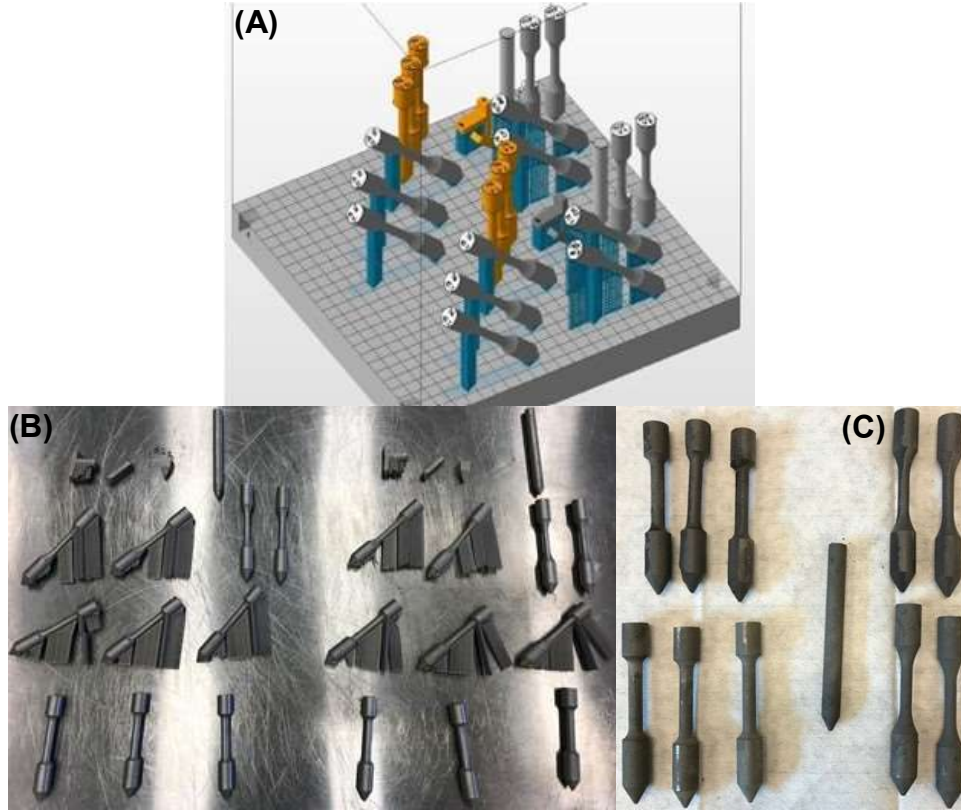


Fig. 5 EOS M290 build layout (A), as-built specimens (B), and post-etch (C).

The resulting stress-strain diagrams for AM IN718 control and sensitization/etch were generated. As expected the effect of build orientation does have an impact on mechanical properties as shown in Figure 6.

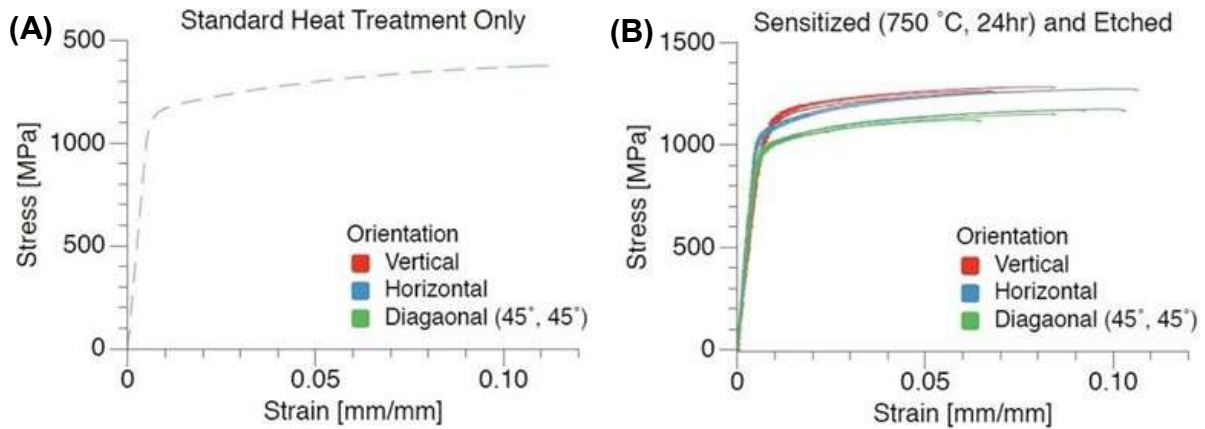


Fig. 6 AM IN718 stress-strain curve comparison between as-built (A) and etched (B) [3].

YS, UTS, and E are similar between specimens considering variation of build orientation, heat treatment, and etching as shown in Table 2. The variation in ϵ and varies widely between the different conditions and orientations. The potential reasons for variance is likely attributed to detrimental build artifacts (i.e. re-coater damage) that created non-uniform surface conditions or variations in the heat treatments schedules or measurement error in the testing process due to the limited number of specimens tested. Repeating the print and post-processing may be required to determine if the change in ϵ is due to undesirable aspects of the build orientation / process or post-processing. Microstructural characterization can also provide additional insight to explain such changes.

Table 2: AM IN718 control and etch median tensile property comparison.

Name	Condition	Orientation	YS _{med} (MPa)	UTS _{med} (MPa)	E _{med} (%)	E _{med} (GPa)
Reference	Control	Vertical	1154.73 ± 3.38	1379.3 ± 1.17	24.23 ± 0.27	184.37 ± 5.52
TN-V	Control	Vertical	1169.28 ± 7.90	1378.61 ± 12.03	10.91 ± 2.72	206.77 ± 3.88
TN-V-E	Etch	Vertical	1193.34 ± 7.22	1426.59 ± 98.28	17.39 ± 9.89	214.63 ± 11.69
TN-45	Control	45°	1179.83 ± 6.14	1330.10 ± 73.28	5.22 ± 4.99	216.39 ± 2.49
TN-45-E	Etch	45°	1199.96 ± 9.76	1368.40 ± 86.07	3.26 ± 2.56	219.25 ± 3.78

Fatigue control specimens with as-built surface finish in the gauge section and etched surface finish specimens were tested according to guidelines established in ASTM E466, “Standard Practice for Conducting Force Controlled Constant Amplitude Axial Fatigue Tests of Metallic Materials”. It was found that differences between control and etch specimens are more related to the specimen build orientation than the etching process. However, it can be seen that there is a slight increase in the number of cycles in the etched specimens, which would be expected with a smoother surface finish. It must be noted that the number of specimens and test conditions were limited and further investigation is needed to generate a complete stress-cycle (S-N) curve.

Table 3: AM IN718 control and etch HCF behavior comparison.

Name	Condition	Orientation	Max Stress (MPa)	Cycles (#)
HCF-V-1	Control	Vertical	517.11	140,190
HCF-V-2	Control	Vertical	517.11	150,965
HCF-V-E-1	Etch	Vertical	517.11	157,524
HCF-V-E-2	Etch	Vertical	517.11	214,814
HCF-45-1	Control	45°	517.11	97,594
HCF-45-2	Control	45°	517.11	124,262
HCF-45-E-1	Etch	45°	517.11	132,878
HCF-45-E-2	Etch	45°	517.11	129,872

C. Microstructural Characterization

Specimen microstructural characterization using optical microscopy was used to determine bulk surface morphology and porosity. Scanning electron microscopy (SEM) was used to obtain high resolution micrographs to evaluate smaller porosity, the influence of the etching process on the microstructure as a function of depth into the specimen, and the elemental chemical composition using energy dispersive spectroscopy (EDS). The primary concern for utilizing the sensitization and etch process is that it will induce deleterious effects on the microstructural and mechanical properties of components. We compare as-built specimens to fully processed specimens in order to assess microstructure evolution as a function of condition. SEM micrographs and EDS maps of the as-built condition show porosity and elemental distribution in Figure 7. The etched specimen (stress relief, sensitization at 750 °C for 24 hours, etching, HIP, solution and age heat treatment) micrographs and spectra are shown in Figure 8. For reference, the nominal IN718 elemental composition is primarily Nickel with 20.5-23 wt% Chromium, 17-20 wt% Iron, 8-10 wt% Molybdenum, and numerous elements below 1 wt%. For the purposes of this study the four primary elemental distributions were compared between the as-built and etched conditions. Comparison of EDS maps show no appreciable change in elemental composition between the two conditions, such as depletion or enrichment that evolve as a function of heat treatment and etching. Previously published work showed that support structure dissolution is extremely sensitive to trace oxygen levels that can promote the formation of a thick oxide layer that acts as a sensitization barrier and consequently inhibits support removal [2], [3]. No substantial surface oxides were present on the surface of either the as-built or sensitized/etched conditions. Figure 9 compares as-built and etched specimen porosity distribution. The as-built condition show minimal porosity and dendritic grains typical for AM. The etch specimen shows higher porosity, which is unexpected since HIP decreases internal porosity, the region was not exposed to the sensitization or etchant chemicals, and etched mechanical properties do not decrease relative to control properties. A likely explanation could be location on the build plate during L-PBF AM but this is speculation and further evaluation is required to determine the cause of increased porosity in the etched condition specimen. It must be noted that when only one metallographic specimen in each condition was evaluated. Additional surface finish and failed mechanical test specimens are currently undergoing metallographic preparation and porosity evaluation.

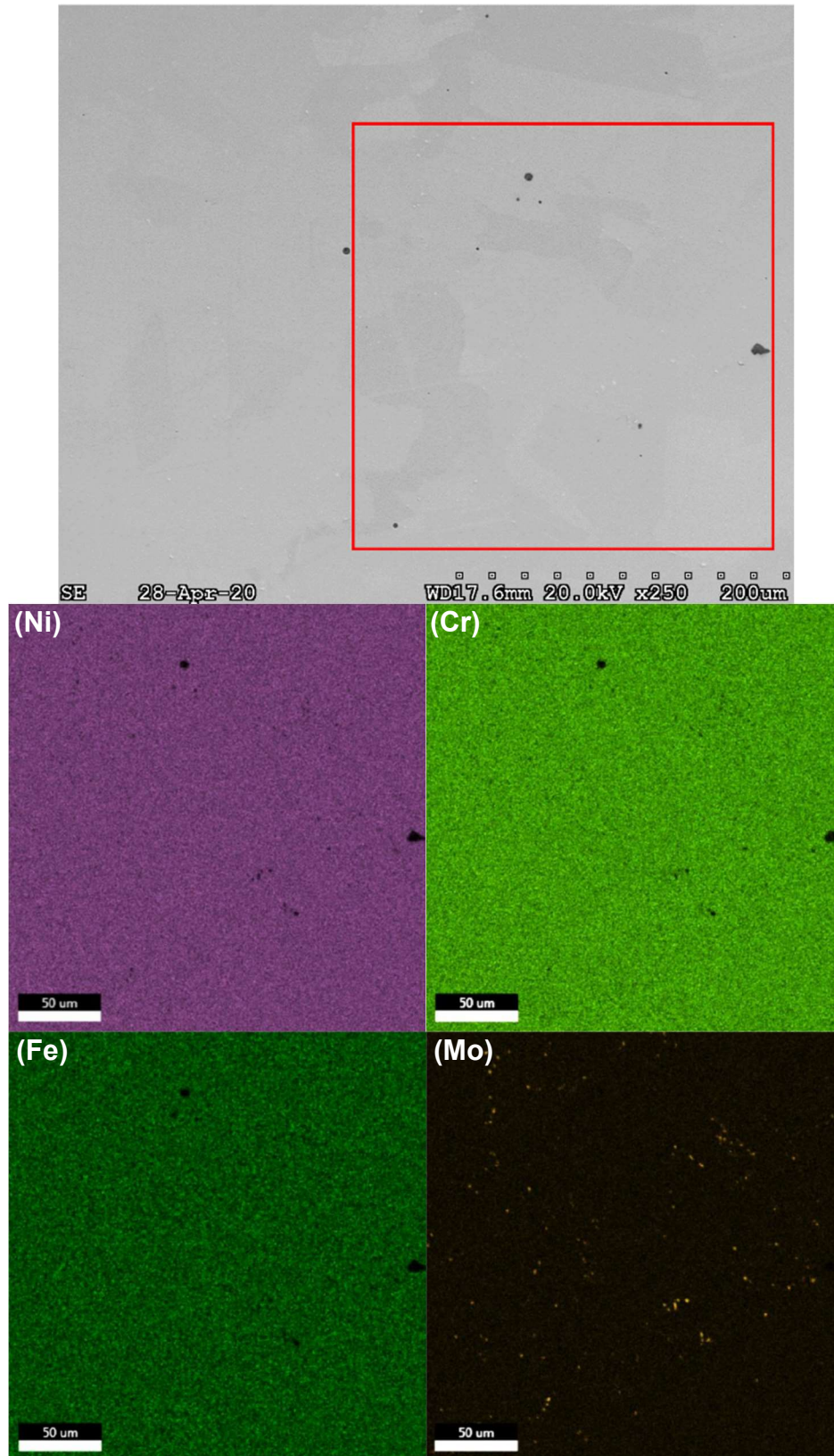


Fig. 7 SEM micrograph and EDS maps of IN718 as-built condition at 250x.

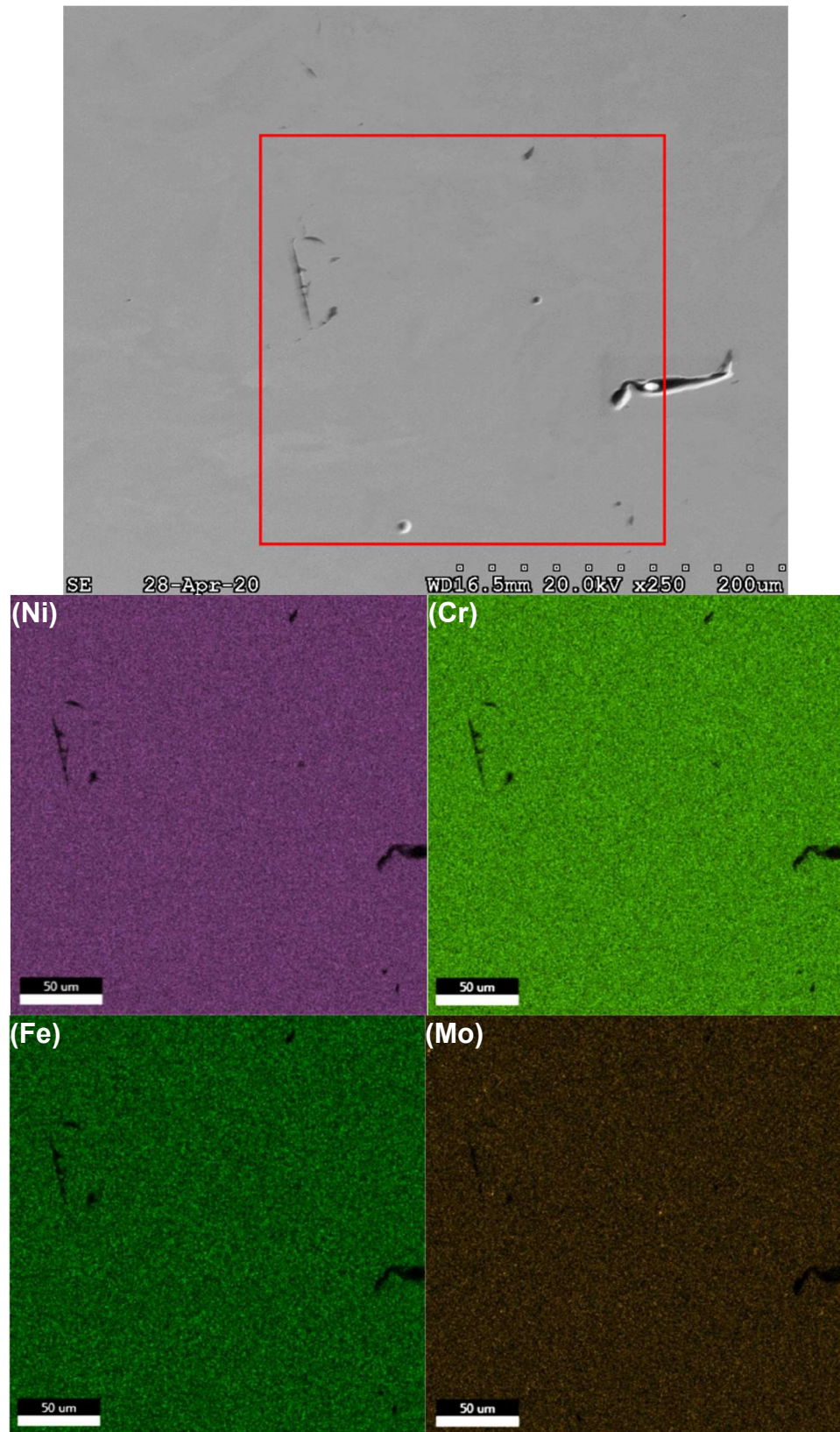


Fig. 8 SEM micrograph and EDS elemental maps of IN718 after stress relief heat treatment, sensitization at 750 °C for 24 hours, etch, HIP, solution and aged heat treatment condition at 250x.

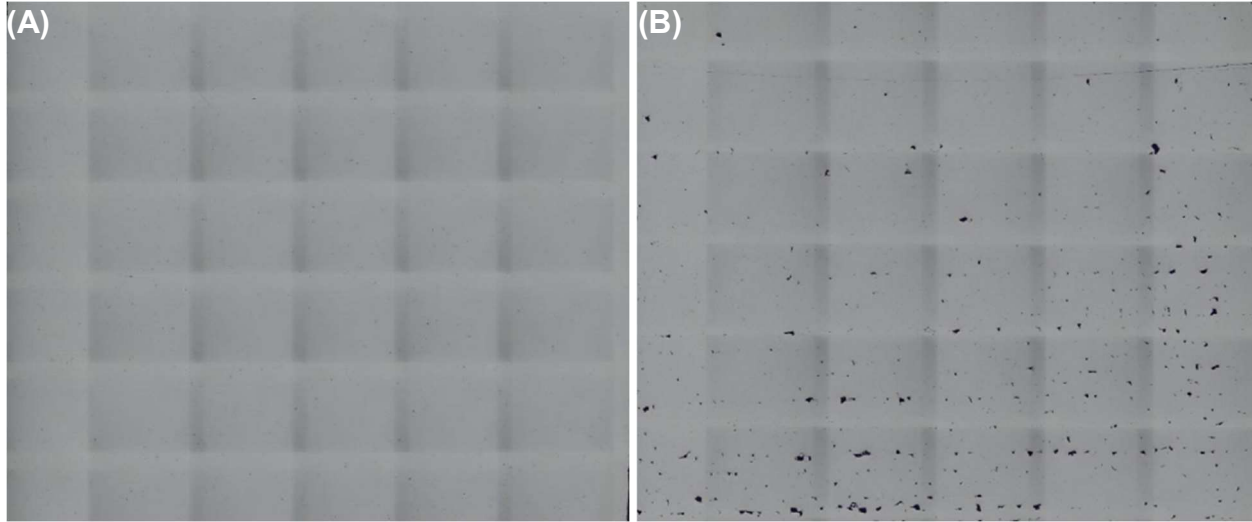


Fig. 9 SEM micrographs of IN718 as-built (A) and etched condition (100x).

X-ray diffraction (XRD) was used to investigate potential phase changes near the surface between the fully heat treated (stress relief, HIP, solution, age) and the dissolution (stress relief, HIP, sensitization, etch, solution, age) conditions. The two specimens underwent metallographic preparation followed by evaluation under XRD. The resulting XRD spectra, as shown in Figure 10, illustrates peaks for the γ Ni-Cr solid-solution matrix phase, which has a face-centered cubic (FCC) crystal structure. In addition, the spectra show peaks for the γ'' Ni_3Nb precipitate phase, which has a body centered tetragonal (BCT) crystal structure. These phases are typical for IN718 in the fully heat treated condition and results indicate that the influence of the sensitization and etch process has negligible impact on subsequent phase content and distribution. No deleterious phase peaks such as δ , carbide or laves phases were evident in the XRD spectra indicating that the heat treatment process was conducted properly in accordance with AMS 5664 specifications. The spectra result are important since the phase type, size, and distribution that are generated during heat treatment are responsible for the expected mechanical properties of the precipitation strengthened alloy IN718.

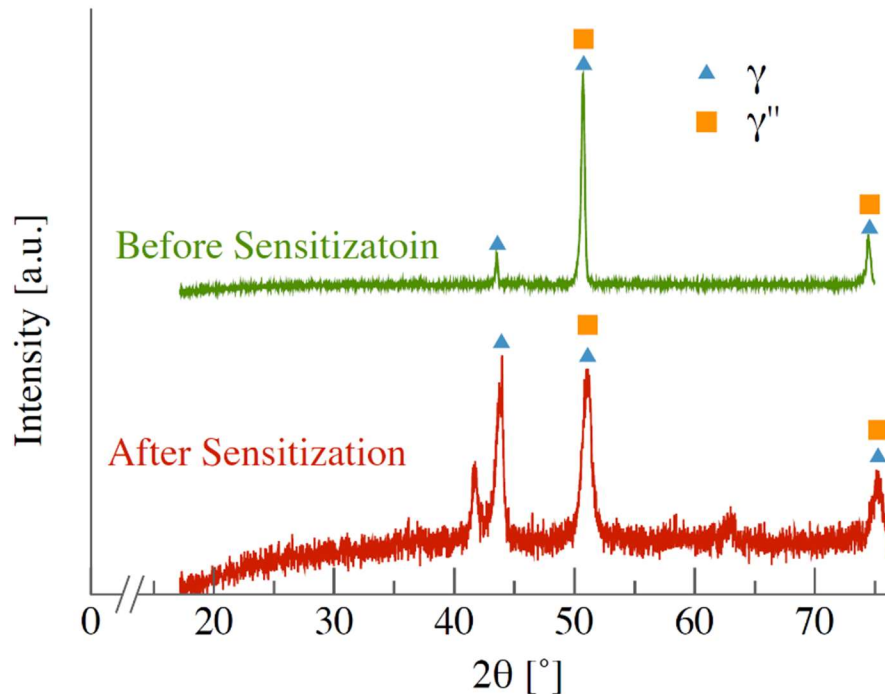


Fig. 10 XRD spectra of AM IN718 showing surface phase evolution between as-built and etched [3].

D. Surface Roughness Characterization

Surface finish specimens in the as-built and etched conditions are shown in Figure 11 and underwent surface roughness (S_a) measurement using a Keyence VR-3200 wide area 3D scanner using a magnification of 80x in super-fine mode. Surface measurement area orientations included “front”, which faces the recoater blade, “back” facing away from the recoater blade, with “up-facing”, and “down-facing” being self-explanatory. Scan data was used to derive S_a as a function of surface angle relative to the Z direction as shown in Figure 12.

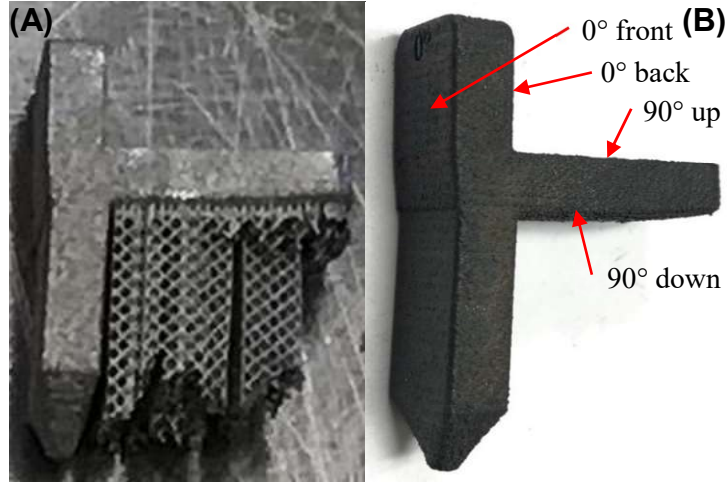


Fig. 11 Surface finish specimen in the as-built (A) and etched (B) conditions.

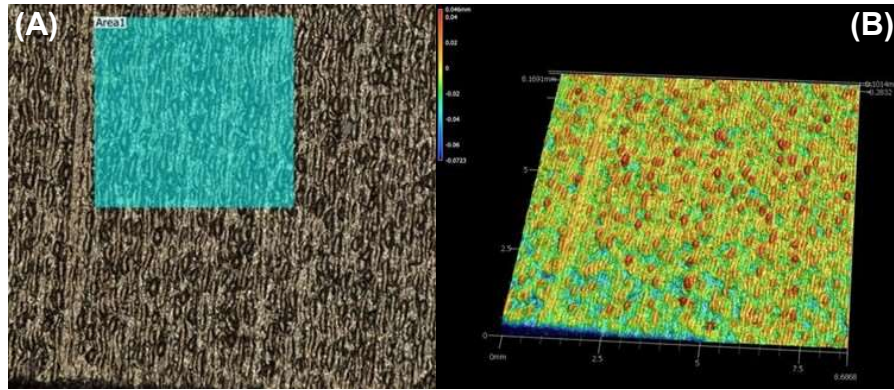


Fig. 12 Pre-etch optical image (A) and scale limited image (B) both at 80x magnification.

As-built surface finish for L-PBF AM parts is dependent primarily on layer thickness, laser focus diameter, and powder particle size distribution (PSD). Table 4 shows the resulting surface finish measures as a function of angle from the Z direction. As expected, S_a varies most with respect to angle and orientation. For example, the vertical surface (0°) facing away from the re-coater blade has the smoothest surface with the 45° down-facing surface having the roughest. The etching process seems to increase roughness in vertical surfaces with decreasing it in down-facing surfaces. This could be a consequence of inter-laminar etching exacerbating the peaks and valleys between build layers but more investigation is required to determine an exact cause.

Table 4: Surface roughness comparison.

Condition	S_a (μm)					
	0°		45°		90°	
	Front	Back	Up-Facing	Down-Facing	Up-Facing	Down-Facing
As-built	12.5	11.1	20.4	41.3	21.1	44.6
Etched	13.7	12	-	-	14.6	40.12

E. Component Trials

Lessons learned from the specimen build and etch trials were used to generate an optimized IN718 support structure etch process that was then applied to segments of the Additive Manufacture Demonstration Engine (ADME) Oxygen Turbo Pump (OTP) stator. The stator segments were printed from IN718 on the EOS M290 at MSFC. The stator blades are thin and their position relative to one another make the support structures semi-inaccessible. It is common practice to utilize segmented perforated block support structures for ease of removal after printing. This support structure type is critical in order to drain the supports of excess powder and the amount of material that must be dissolved away, which decreases the amount of consumables used in the sanitization and electrochemical dissolution process. The immersion method was used on the stator segments, which allowed for uniform distribution of the sensitization agent throughout the complex blade and support structure geometric features. After sensitization and etching the stator segments were sent to MSFC for evaluation. The support structures were removed; with isolated support remnants removed with grit blasting. However, the surface finish of the bottom of the blades was noticeably rougher than the top surface as shown in Figure 13. It is thought that additional optimization of the etch process can help to improve etching at the support structure to component contact points that was responsible for the rough surface finish. For most components the roughness would be an improvement over the as-built surface finish but unfortunately for turbo-machinery experiencing fatigue environments additional surface finish modification is required (i.e. slurry hone and electro-polish).

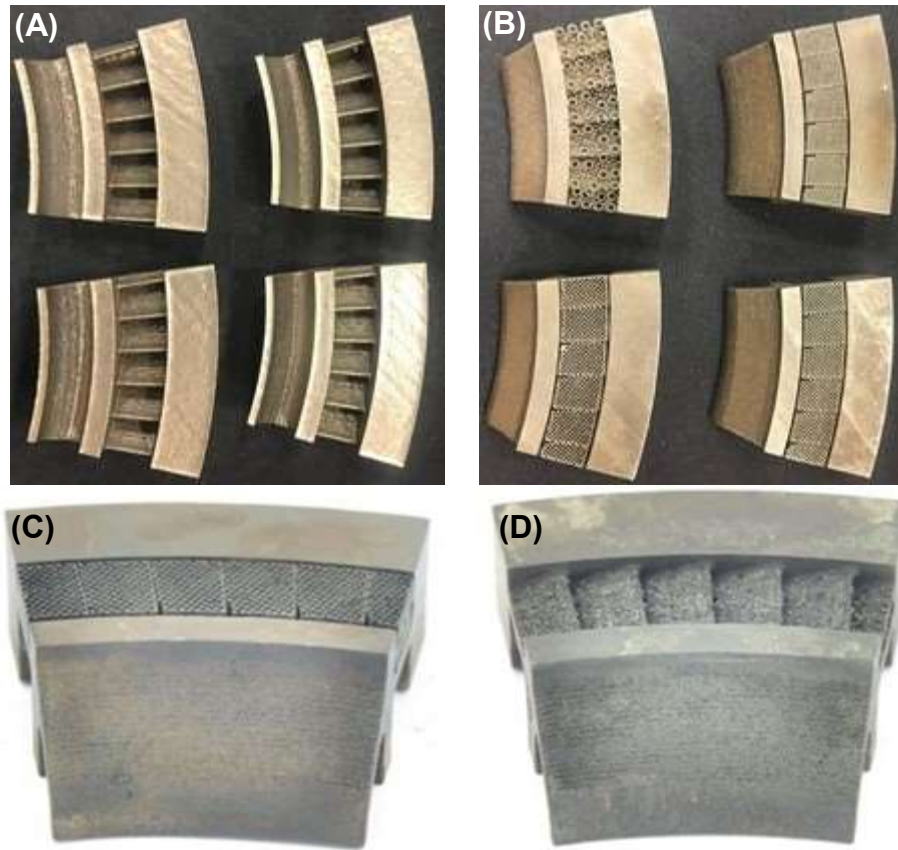


Fig. 13 AMDE OTP IN718 stator segments pre-etch (A, B, C) and post-etch (D). Supports were not fully dissolved but sufficiently weakened to remove via grit blasting.

One stator segment was sectioned, mounted, ground, and polished in order to evaluate the impact of the etching process on the thin blades within the stator. The stator specimen underwent SEM/EDS and the resulting images show little to no trace of support structure contact points as shown in Figure 14. As mentioned previously, oxide layers can act as sensitization barriers, which may have been responsible for the higher surface roughness.

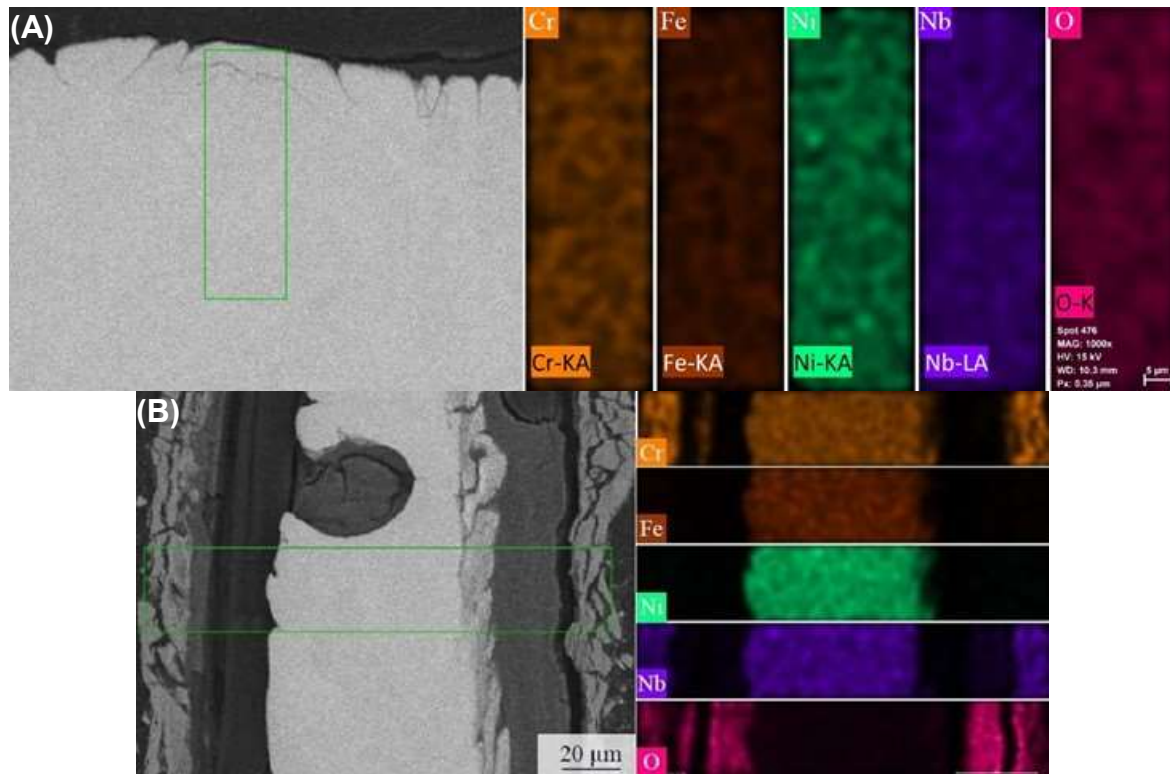


Fig. 14 SEM-EDS maps of post-sensitization stator part surface (A) and support structure (B) [3].

The final stage of development was to scale-up the process to a prototypic size component in order to identify scale-up limitations as well as uniformity of support structure removal along a relatively large component. The AMDE OTP stator size was printed as shown in Figure 15 and constituted roughly half of the EOS M290 build volume. In order to facilitate shipping logistics the stator underwent stress relief heat treatment and was removed from the build plate before shipment to CSM. The support structures were fully removed, with similar surface finish to what was documented with the stator segments. Overall, the process for bulk support structure removal has been established for small to moderate size components but will require additional optimization in order to improve surface finish. Understanding the mechanisms for such differences in dissolution effectiveness



Fig. 15 AMDE OTP IN718 stator with blades over perforated block support structures.

IV. Conclusion

Electrochemical dissolution of AM IN718 support structures has been shown feasible with some process optimization initiated. The etch process was found to have minimal changes in microstructural, tensile, and HCF properties with moderate improvement in surface finish condition. It must be noted that the support structure dissolution process should be limited as a measure of last resort due to increased cost and schedule required to complete the process. Examples of appropriate application include components with geometric features that cannot be optimized for AM, such as small aerodynamic surfaces (fins and blades) or inaccessible internal passages where supports cannot be reached for mechanical removal. Higher fidelity characterization of AM IN718 mechanical (particularly HCF), microstructural, and surface finish as a function of etch condition should be conducted. Formulations for support structure etching of standard and emerging AM alloys should be developed and optimized in order to enable broad-scale industrial adoption.

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