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14. ABSTRACT Additive manufacturing has been highlighted in the DOD as a means to reduce operational costs (production and storage costs) on parts that are highly complex and expensive. For example, the ability to leverage AM to generate parts on demand with no need for post-processing eliminates the substantial costs associated with the storage and care of parts in quantity. The advantage of AM is greatly compromised if the parts' corrosion behavior results in catastrophic failure in the field. Recent research indicates that the origin of corrosion in AM parts is closely related to the processing conditions of AM materials. The key to unlocking improved corrosion resistant parts directly out of the AM systems relies on precise control of machine parameters and input materials. The focus of this work is to investigate both machine parameters and feedstock optimization to develop robust 316L materials directly out of the AM system while eliminating the need for additional processing.						
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Please refer to:
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Dear Dr. Perez:

The Johns Hopkins University Applied Physics Laboratory (JHU/APL) is pleased to submit the enclosed Final Technical Report for the “Corrosion Investigations of Additively Manufactured Alloys” project, JHU/APL Task FGC55, for the reporting period of July 1, 2017 to July 30, 2018, in accordance with requirements of the subject award.

If you have any questions or comments regarding this report, please free to contact me at 240-228-7681 or email steven.storck@jhuapl.edu

Sincerely,

Original signed by,

Steven Storck
Project Manager

Enclosure

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Corrosion Investigations of Additively Manufactured Alloys

Final Technical Report

Award #: N00014-17-1-2576

Submitted by,
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Office of Naval Research, SEA Platforms & Weapons Div.

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Reporting Period: July 1, 201 to July 30, 2018

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List of Acronyms

AM – Additive Manufacturing

DoD – Department of Defense

DOE – Design of Experiment

EDS - Energy Dispersive X-Ray Spectroscopy

EOS – Electro Optical Systems

KH – Keyhole

LOF – Lack of Fusion

RBV- Reduced Build Volume

SLM – Selective Laser Melting

X-Ray CT – X-ray Computed Tomography

SUMMARY OF EFFORTS

The primary objective of the N00014-17-1-2576 effort was to improve corrosion resistance in Additively Manufactured (AM) 316L Stainless Steel. To achieve this objective, we utilized a dual approach of feedstock modification and optimized processing parameters.

Feedstock Modification

- Initial proof of concept surface treatments *using Cerium as an on-demand corrosion inhibitor on AM 316L showed a 74% improvement in corrosion performance* when compared to non-treated AM 316L.
- 316L feedstock powders were modified by doping with 0.2 wt% Ce, resulting in materials that contain the desired volume fraction of Ce at the surface. Chemical treatments of the feedstock with Ce-containing stock solution enabled highly tailored surface chemistry. This two-part solution treatment can be optimized through reactant-limited kinetics in order to maximize effectiveness of the passive corrosion inhibitor for the AM parts.
- New AM build techniques based on a Reduced Build Volume (RBV) were established to minimize the demand on powder quantities for custom developed powders. This will enable *cost-effective powder development with a two order of magnitude reduction in required power volume*. Powder costs were reduced from \$3060 per run to ~\$35 per run (\$153 per kg based on 316L EOS powder costs).
- Novel feedstock powders were demonstrated to be amenable to laser consolidation using Selective Laser Melting (SLM) using the Renishaw RBV.

Optimized AM Processing Parameters

- At the onset of the effort, it was quickly realized that *industry-established AM processing parameters seriously impair resistance to corrosion in 316L*. Furthermore, conventional electrochemical protocols such as those described in ASTM-G61 used in evaluating pitting corrosion are unsuitable for AM 316L, for reasons discussed in the following bullet. We were able to identify alternative processing parameters and improved electrochemical techniques which directly address the primary objective described above.
- The ASTM-G61 protocol was evaluated to study the pitting corrosion potential. It was found that no pits form under the slow scan rate required for the test, and corrosion initiates at the edge of the cell and rapidly covers the surface. Under these findings a *pitting potential cannot be reported since the mechanism for corrosion is not pitting*.
- Collaborative discussions with Rob Kelley and Sebastian Thomas indicate that reduced sulfur in the AM feedstock limits the formation of MnS, a pit initiation compound.
- To better characterize pitting, several other corrosion tests were evaluated: fast potentiodynamic, potentiostatic and galvanostatic pulse-transients. *Potentiostatic pulse-transient techniques were established as the best approach for identifying pitting probability in AM 316L stainless steel* because the energy pulse occurs at a voltage beyond edge initiation. The pulse and hold test also allows a quantifiable measurement of material loss through Faraday's law by measuring Coulombs during the experiment.
- A design of experiment (DOE) approach was utilized to study processing parameter effects on corrosion performance. Energy input was fixed to maintain production of fully dense (>100% at 13 micron resolution) material while varying processing parameters,

enabling a sensitivity study. Critical machine parameters (Power, Laser Speed, and Hatch Spacing) were varied to determine the impact on corrosion behavior.

- X-ray computed tomography (XRCT) was used to quantify defect density in parts produced. For continuous laser materials, *no defects >13 microns in diameter were detected in any of the samples.*
- A false color mapping technique was established to highlight corrosion sites. This technique enabled identification of corrosion sites versus manufacturing defects (i.e. porosity).
- A *direct correlation was established between laser speed and material loss due to corrosion.* Reducing laser speed by 33% (which is only a 7.8% increase in build time) results in a 76% improvement in corrosion performance.
- Compared to corrosion in conventional 316L, *microstructure attack was found to be active as a corrosion mechanism in AM 316L.* The degree of microstructural attack in AL 316L samples was found to be correlated with pitting frequency. Initial evidence suggests that sensitization is occurring from microstructure attack observed in some of our test samples.
- Chemical composition was analyzed using Energy Dispersive X-Ray Spectroscopy (EDS) to investigate local chemistry, potential segregation and impact on corrosion performance. *Segregation of chromium was identified as critical in contributing to poor corrosion performance.*

Conclusions

- Modified feedstock can be produced with a number of low cost methods enabling custom alloys tailored for corrosion performance.
- Surface modifications are incorporated into the selective laser melted deposits and dispersed uniformly through the volume.
- Initial surface treatments result in a nearly doubled corrosion potential, indicating the power of Ce treatments.
- Processing parameters have been varied to establish fundamental control over the solidification behavior of unmodified AM 316L.
- Reduced laser speed is critically linked to improved pitting corrosion and a reduction in grain boundary attack.
- A method to evaluate the pitting performance of AM 316L was established, and indications of sensitization and grain boundary attack were found to be evident.

Remaining Challenges and Opportunities

Building on the methods developed and results attained during the year 1 initial effort, there are several opportunities for further investigation that can contribute to further elucidating AM 316 L corrosion mechanisms and development of corrosion resistant alloys.

- **Feedstock Modification**
 - Use oxide reduction reactions to convert Ce^{4+} to Ce^{3+} , the passive corrosion inhibiting form of Ce, via a hydrogen forming shielding gas.
 - Investigate the impact of other dopants, such as SiC, on crevice and sensitization problems, to promote pH stabilization at crevice-prone locations. In combination with Ce, these additional dopants are believed to improve solidification behavior

and stabilize grain structure, based on preliminary efforts conducted with JHU/APL internal funds. This improvement in solidification and nucleation in combination with the passive corrosion capabilities can dramatically improve processing and corrosion performance.

- Evaluate scalability of dopants to gas atomization manufacturing.
- **Processing Optimization**
 - Optimize thermal history and processing to decrease sensitization, in a collaborative effort with the Kelly group at University of Virginia (UVA).
 - Evaluate the impact of laser solidification mechanisms on meltpool and grain boundaries, which are the dominating microstructural elements susceptible to corrosion in AM 316L.
 - In the future, there is potential to control the thermal history during fabrication to dissolve chrome carbides, which have been shown to be a limiting factor of AM materials by other ONR program researchers.
 - Further investigation is needed to fully optimize corrosion behavior based on speed as the critical variable. Future efforts in this area should consider multiple forms of corrosion with cross program collaboration to promote the most optimal corrosion performance.

Introduction

Additive manufacturing has been highlighted in the DOD as a means to reduce operational costs (production and storage costs) on parts that are highly complex and expensive. For example, the ability to leverage AM to generate parts on demand with no need for post-processing eliminates the substantial costs associated with the storage and care of parts in quantity. The advantage of AM is greatly compromised if the parts' corrosion behavior results in catastrophic failure in the field. Recent research indicates that the origin of corrosion in AM parts is closely related to the processing conditions of AM materials. **The key to unlocking improved corrosion resistant parts directly out of the AM systems relies on precise control of machine parameters and input materials.** The focus of this work is to investigate both machine parameters and feedstock optimization to develop robust 316L materials directly out of the AM system while eliminating the need for additional processing.

Evaluation of the corrosion response of standard 316L produced via additive manufacturing

The following section will discuss how to control solidification behavior of AM materials through critical additive manufacturing parameters and relevant corrosion testing techniques for AM 316L to measure pitting corrosion behavior.

Additive Manufacturing of 316L and critical processing parameters

The process of producing material via selective laser melting (SLM) is governed by the energy input, which is given in equation 1[1-7].

$$E = \frac{P}{V*H*t} \quad \text{EQ1}$$

E is energy density, P is laser power, V is scan velocity, H is hatch spacing, and t is layer thickness. This equation incorporates some of the critical parameters for bulk AM deposits. The equation has been used to accurately identify void space of AM deposits. Three critical defect zones exist when processing AM material: 1) Lack of fusion (LOF) porosity, formed when not enough energy is input and powders fail to fuse; 2) Keyhole (KH) porosity, formed when too much energy is input and powders are vaporized resulting in gas porosity; and 3) the fully dense zone with no porosity. The relationship between energy input and defect types can be seen schematically in **Figure 1: Shows the processing range of AM materials with the optimal fully dense range highlighted in green and the Lack of fusion and Keyhole zone highlighted in red.**Figure 1.

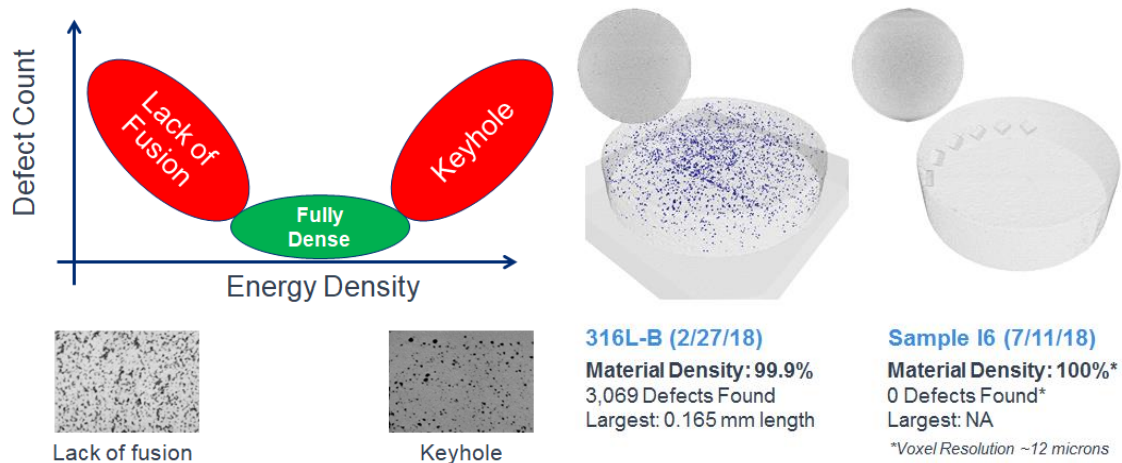


Figure 1: Shows the processing range of AM materials with the optimal fully dense range highlighted in green and the Lack of fusion and Keyhole zone highlighted in red. An X-ray CT scan showing keyhole defects at a resultant density of 99.9% is shown next to a fully dense sample. Even samples with 0.1% porosity have a significant number of defects. All samples in this study are 100% dense at 13 micron resolution.

It is important to note that many combinations of processing parameters can result in fully dense material. Machine vendors strive to produce fully dense materials with mechanical performance as a secondary concern. Typically, stress and strain are the primary objectives when mechanical properties are considered. However, **machine vendors do not currently consider corrosion performance when they are developing parameters, so there is potential for accelerated corrosion, even for parts that meet process control standards such as density and strength.** It is not uncommon for machine vendors to adapt parameters for improved performance from researchers publishing findings in the literature. A strong example of this is EOS changing aluminum processing parameters in 2017-2018, possibly due to findings in the scientific community on surface roughness and strength. Investigating and correlating processing parameters to corrosion performance could result in a similar adaptation of recommended parameters.

One of our primary goals was to explore the manufacturing space of 316L to determine if the stock manufacturing conditions are optimal for corrosion. Additionally, it was of interest to determine which machine parameters have the largest impact on corrosion, while maintaining part performance. Finally, these insights were used to develop a parameter space for optimizing corrosion performance. Table 1 shows the parameter space developed for the primary investigation of processing parameters effects. In this effort, to ensure fully dense material was produced, the energy density was held constant at 100 J/mm^3 . Layer thickness was also held constant to optimize sample production. This enables direct comparison of the manufacturing conditions and elucidation of those that influence corrosion performance. This is the ***first study to evaluate critical processing parameters in the fully dense regime with respect to improving corrosion performance of AM alloys.***

Table 1: Processing parameters used for 6-sample sensitivity study. Two variables were adjusted for processing of each sample in order to hold energy density and layer thickness constant across all. The red and green highlighted cells indicate the adjusted variables for each sample, and the direction of the parameter change (red = 20% increase, green = 20% decrease) relative to control vendor parameters.

	Power	Velocity	Hatch Spacing
	(W)	(mm/s)	(mm)
Control (0)	195	1083	0.09
1	234	1300	0.09
2	156	866	0.09
3	151	1083	0.07
4	195	1380	0.07
5	240	1083	0.11
6	195	885	0.11

After producing samples, porosity was evaluated to confirm fully dense material was produced. All 7 conditions developed for the corrosion samples (100% dense) in Table 1.

Corrosion experimental setup

The goal of this effort was to study the pitting corrosion in AM 316L. Four techniques were evaluated, which are outlined in

Table 2.

Table 2: Corrosion test techniques comparison

Technique	Outcome	Crevice vs. Pitting	Remarks
Slow Potentiodynamic Scan (10 mV/minute)	In 316L, the technique identifies the potential where crevice corrosion starts	Crevice corrosion dominates over pitting	Not useful in establishing pitting potential
Fast Potentiodynamic Scan (600 mV/minute)	Identifies the potential at which pitting begins	Pitting away from the edge (crevice) is easy to identify	Helps establish potential above which pitting may occur
Potentiostatic Pulse-and-Hold	At the pre-identified optimum potential, pitting dominates over crevice	Rate of pitting is comparable or higher than rate of crevice	Helps compare samples' susceptibility to pitting corrosion
Galvanostatic Pulse-and-Hold	Potential raises sufficiently anodic and causes pitting before crevice starts	By selecting the hold-time, crevice may be completely avoided	Pits may not grow large before crevice starts

Initially, the ASTM-G61 protocol was explored to evaluate pitting potential (Technique 1,

Table 2) [9]. Unfortunately the slow scan rate of 10 mV/min resulted in edge-dominated or crevice-type corrosion (**Figure 2**). Several techniques were explored to minimize edge effects such as potting the samples in epoxy and sealing the interface with lacquer (**Figure 3**)[10]. None of these attempts resulted in eliminating crevice/ edge dominated corrosion for the ASTM-G61 protocol, which resulted in the inability to measure pitting corrosion using this technique.

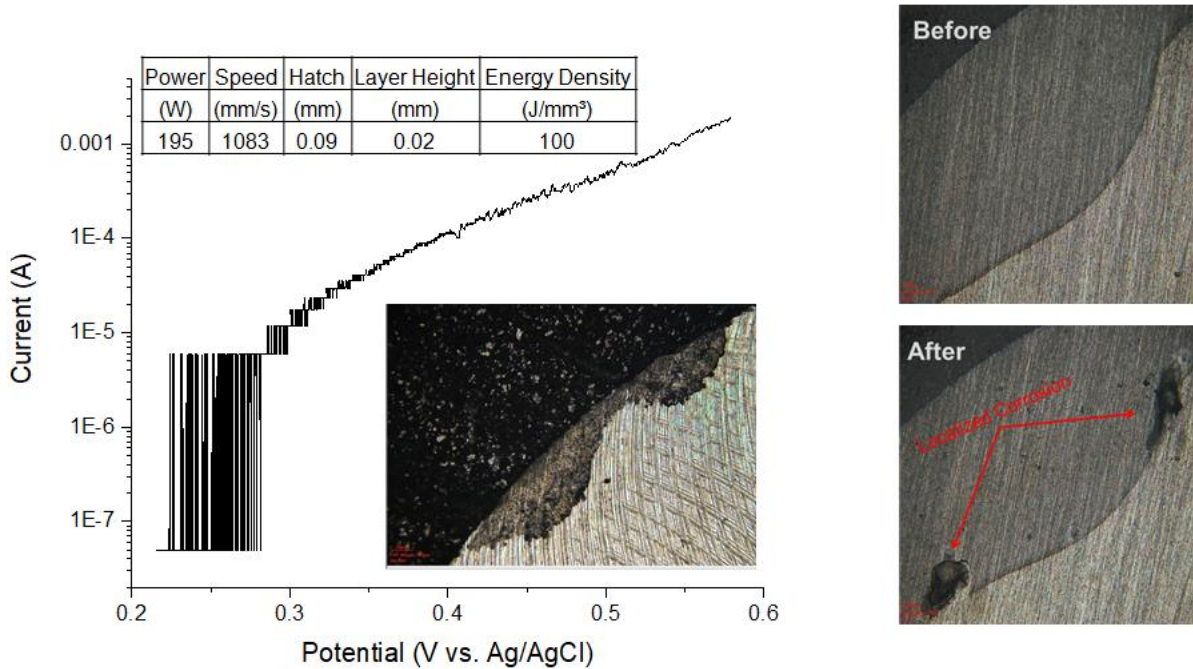


Figure 2: Micrographs showing the edge of the sample after epoxy and lacquer have been applied, and revealing the corrosion products at the edge. The samples follow a Tafel law shown in the graph of current v potential which does not represent pitting.

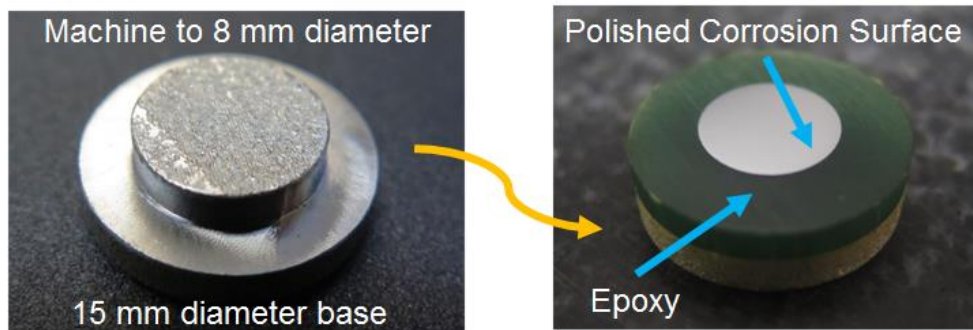


Figure 3: Photographs showing the embedded epoxy technique to minimize edge effects

In order to evaluate the preference for edge or crevice corrosion could be overcome, the scan rate was increased to 600 mV/min (Technique 2, **Table 2**). The result was the ability to identify pitting potential where small pits are observed in the center section of the sample as desired (**Figure 4**). In this case, the nucleation of crevice corrosion is quickly passed, enabling pitting corrosion to be observed. While this technique enables a pitting potential to be observed, it is very difficult to capture a comparable condition for all samples. In order to obtain the desired outcome of being

able to compare all samples under equivalent conditions to establish which parameters most impacted pitting corrosion, a potentiostatic test was completed with a voltage of 1.65 V for 10 min (Technique 3, Table 2). In all cases, pitting corrosion was observed. Since all samples underwent the same corrosion potential, mass loss could be calculated and compared using Faraday's law. The results of the testing can be observed in Figure 5 with a false red color used to highlight corroded areas. The false color map highlights some of the global changes in corrosion response and the mass loss can be measured through Faraday's law. The most extreme samples, 2 with lowest material loss and 3 with highest material loss, show very different corrosion response even though they have identical energy inputs. **This highlights the importance of optimizing parameters across a wide range of physical requirements including corrosion behavior.**

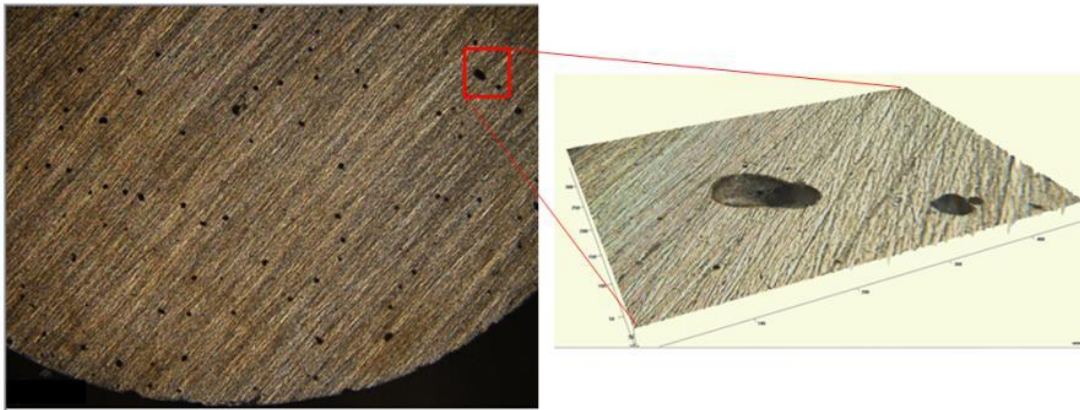


Figure 4: Micrographs showing the results of the fast potentiodynamic scan with pitting corrosion through the test section.

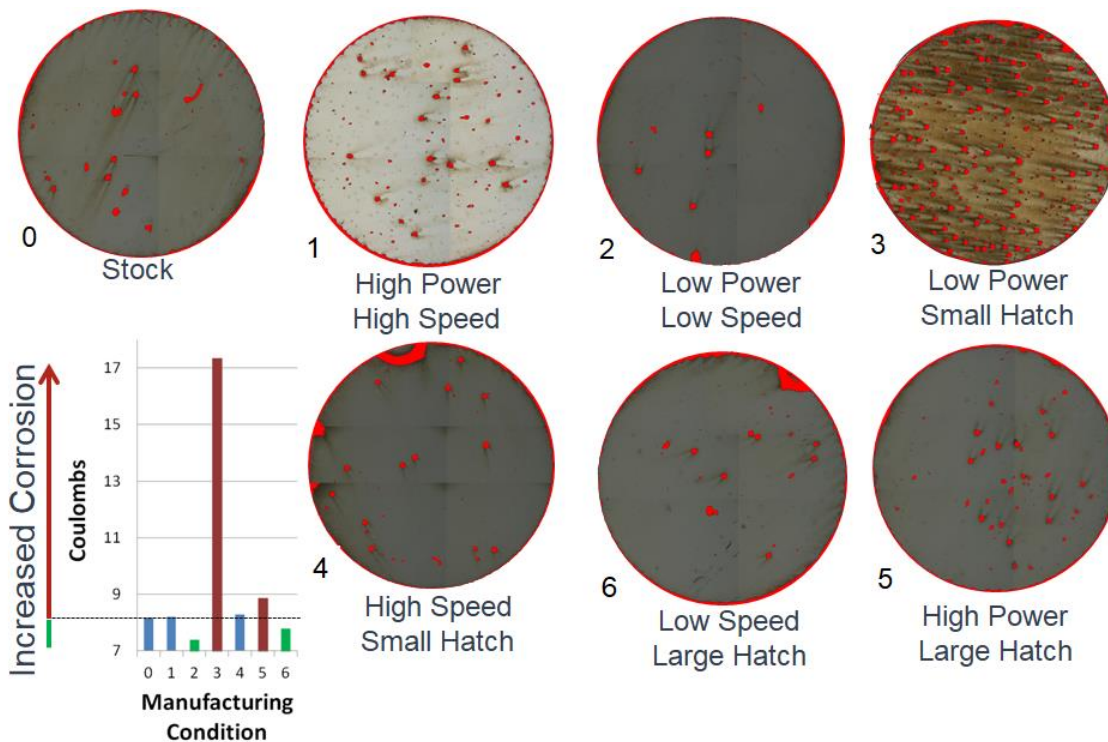


Figure 5: Shows measured pitting corrosion for all samples including the control.

Microstructure of corroded samples

In order to determine the mechanisms for which the AM 316L materials corrode, a scanning electron microscopy (SEM) technique was used to look at areas of the sample both inside and away from areas of classical pitting corrosion. This method reveals some interesting results with respect to the bulk material away from pitting locations (Figure 6). In this image it is possible to see AM-specific features (i.e. melt pool boundary and cellular microstructure) being selectively attacked, indicating the potential for alloy element segregation and sensitization directly out of the AM system. This indicates that the corrosion performance may not be governed by conventional mechanisms of wrought materials. The cellular attack indicates localized corrosion occurs on the length scales that dominate material formation in the additive manufacturing process, highlighting the importance of process parameter control. Cellular attack and pitting corrosion were shown to be significantly reduced in samples (2 and 6) with slower traverse speeds. This improved corrosion performance can be explained because reducing laser traverse speed extends the time the 316L material remains in the melt, thus increasing the time for equilibrium chemistry to be formed.

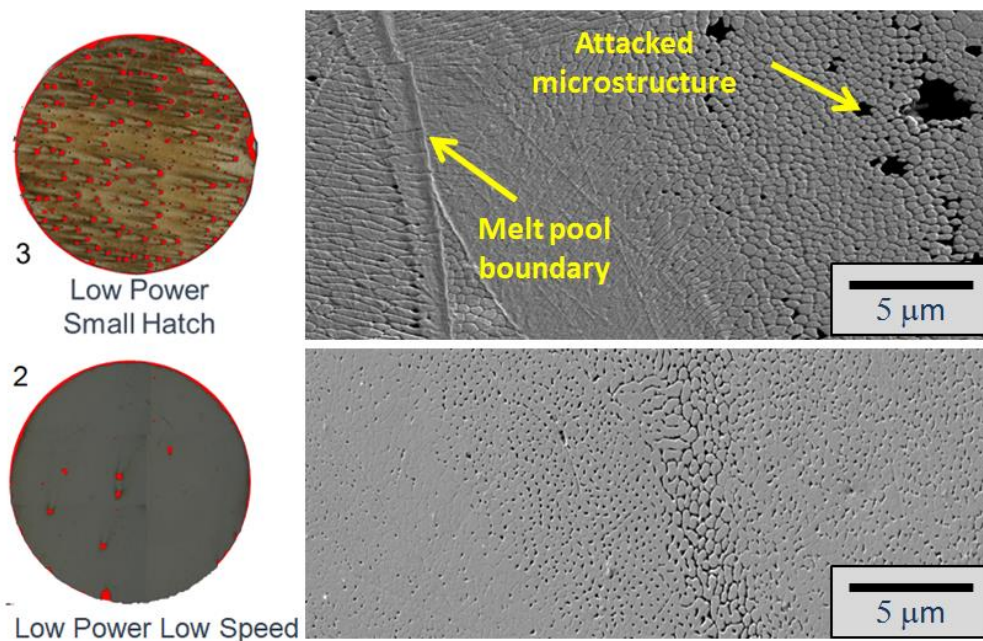
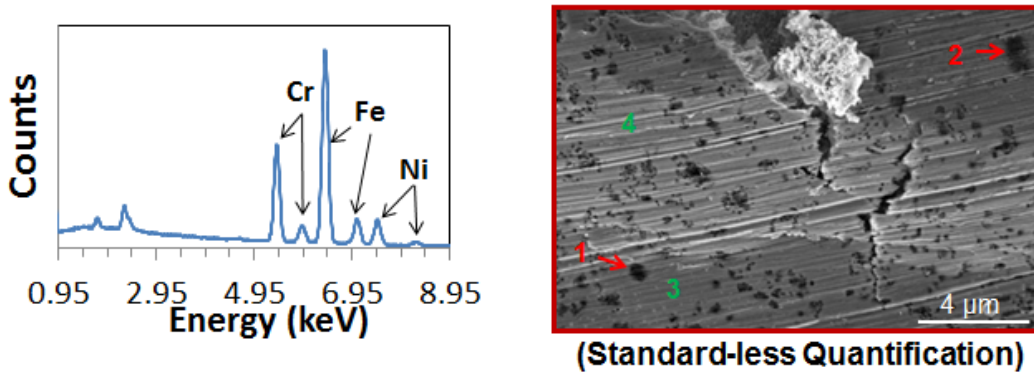


Figure 6: Micrographs showing the localized micron structure attack in areas even outside of pitting.

Chemical Analysis of manufactured samples

To further understand the driving force for the selective microstructure attack, EDS was used to evaluate the local chemistry of the samples. The results strongly indicate localized segregation of alloying elements due to the rapid solidification behavior of the AM process. The chromium concentrations in the zone near corrosion products are rich in chromium, whereas the zones void of corrosion are in the acceptable range of chromium (Figure 7). Localized chromium concentration at the grain boundaries is known to result in selective attack of the grain boundaries [11], and the trends observed in this work further support this observation. However,

in samples with reduced traverse speed, a more stabilized chemistry is achieved (Figure 6) in final samples since the liquid lifetime of the material is extended and diffusion of alloy elements improves. Thus, in order to control this from a material formation process without additional post processing like heat treatments, the laser speed can be tuned to optimize the alloy element distribution.



Element	Powder	Corroded (1)	Corroded (2)	Not Corroded (3)	Not Corroded (4)
Iron (Fe)	62.5	63.7	63	63.9	63.7
Chromium (Cr)	18.6	20.8	20	17.6	17.9
Molybdenum (Mo)	2.77	1.5	2	2.7	2.1
Manganese (Mn)	1.65	2.5	2.2	1.8	1.9
Nickel (Ni)	14.0	10.6	11.5	13.5	10.6

Figure 7: Corrosion is prone in areas of high chromium and low molybdenum indicating the possibility of alloying element segregation in the manufacture recommended parameters (condition 0).

Critical machine parameters to optimizing corrosion behavior

After inspection of the material formation and processing parameters, the hypothesis was that reduced laser processing speed enabled more time in the melt to enable better distribution of alloying elements. The results show significant reduction in corrosion of the material with reduced laser traverse speed (Figure 8). This indicates that an optimal parameter set exists to enable more optimal performance of AM 316L, balancing density, mechanical behavior and corrosion behavior. While the reduction in laser speed will increase build time, the increase is minimal since the recoating step has a much more significant impact on build time. Going forward, build time can be reduced by increasing layer height, which will extend liquid lifetime and should further improve the alloy element distribution. In addition, by increasing the layer height, sensitization should be minimized by reducing the number of times material is remelted. Lastly, meltpool boundaries will be reduced, which will be beneficial since they have the highest cooling rates and subsequently the highest probability of alloy element segregation. Therefore, by optimizing layer height, it is possible to both maximize corrosion performance and minimize build time.

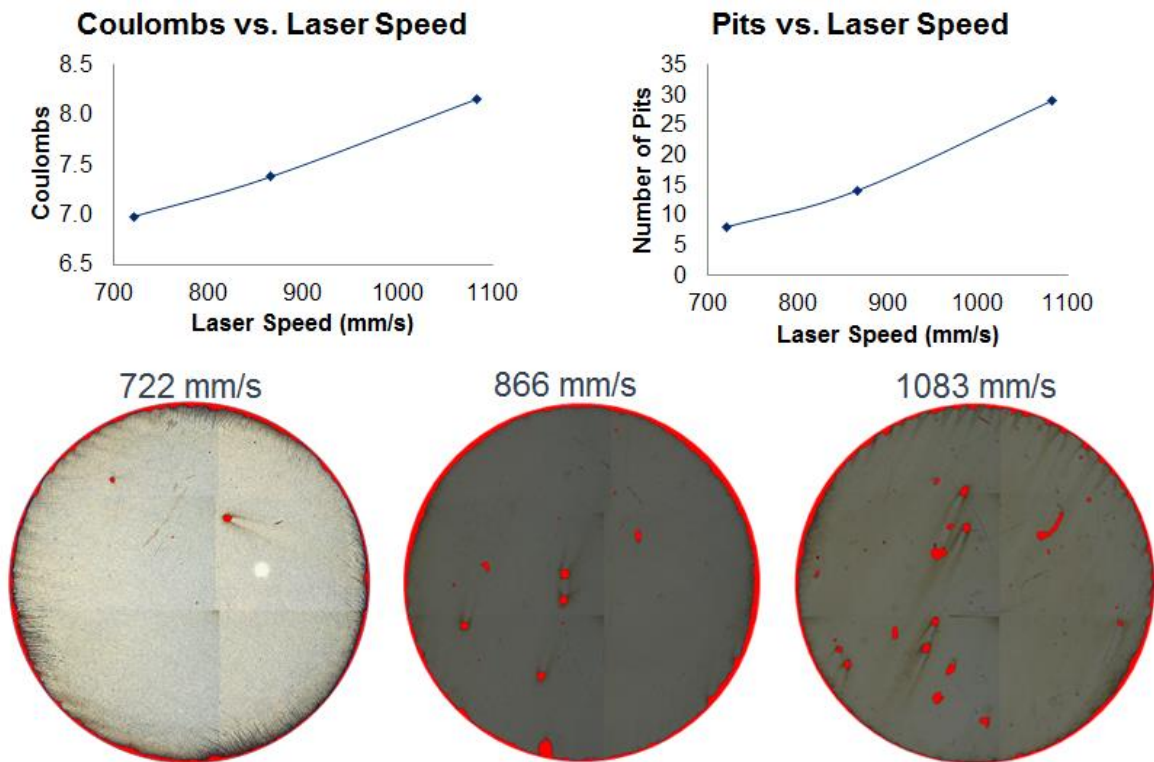


Figure 8: Shows the impact of reducing laser speed on corrosion response. A reduced laser speed results in minimized corrosion.

Although pitting corrosion was the focus here, it is likely that a better distribution of alloying element and grain/meltpool structures will result in significantly improved behavior across the spectrum of corrosion types. This is because alloy elements like chromium are critical to the corrosion performance of 316L through passivation of the material. It has been shown that one of the larger problems for AM 316L is sensitization, which results from the formation of chrome carbides [11]. If processing parameters can be optimized to remove chrome segregation and/or dissolve the chrome carbide at the grain boundaries, significant improvements to sensitization are likely. Significant reductions in grain structure attack were achieved in this study by reducing traverse speed. This likely will extend to a reduction in grain boundary attack, meaning sensitization could be minimized. Investigation of extension the findings from this work to other corrosion types is of interest for future work.

Surface Treatment of AM Powder Feedstock for 3D Corrosion Mitigation

Theory of surface modification

While processing parameter optimization can dramatically improve the corrosion performance as demonstrated above, revolutionary improvements independent of AM systems can be developed with modified powder. The goal of this portion of the effort was to modify the surface of the stock AM 316L powder so that a corrosion inhibitor is integrated to the material and part. This material concept would alleviate the most common shortcoming of the conventional method of surface coating; once the surface coating is scratched or damaged, the structure is prone to failure. By incorporating the corrosion inhibitors throughout the volume, corrosion performance

of the material can be dramatically improved despite any wear during use. The theoretical approach is shown in Figure 9.

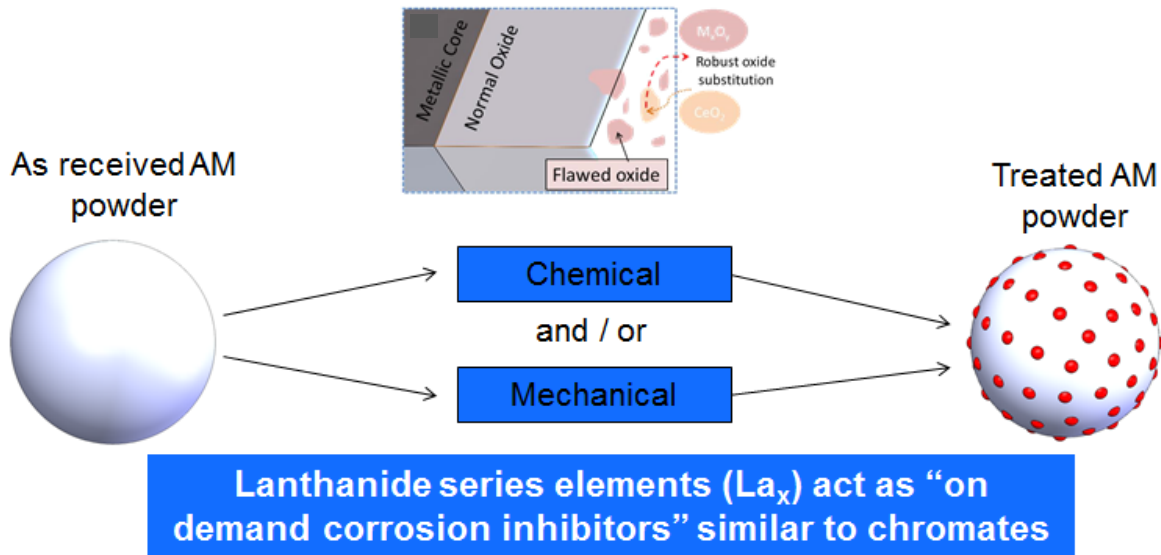


Figure 9: Schematic showing the method for applying corrosion inhibitors to the surface of the AM feedstock.

Lanthanide class elements, such as cerium, have natural corrosion inhibiting activity. The idea is that once laser-processed, the cerium would be distributed through the volume of material, but only become active when a corrosion event is triggered initiating passivation in the film. This is similar to how chromates work, however lanthanides do not have the same environmental challenges and are not toxic. Figure 10 shows the potentiodynamic scan for an untreated and treated 316L stock sample. A 74% improvement in pitting potential, shifting from 0.63 V to 1.1 V, was realized in comparison to standard 316L.

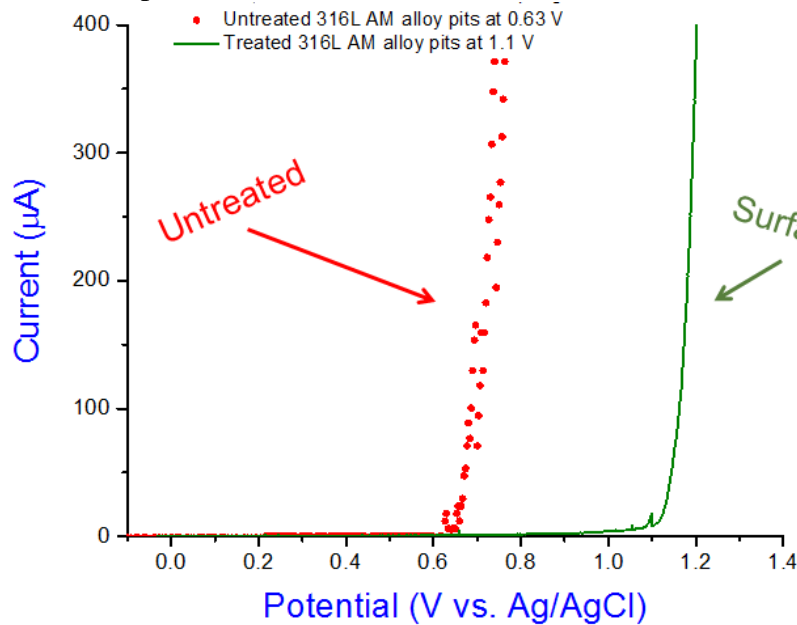


Figure 10: Plot showing electrochemical response of a Ce-treated sample compared to the standard 316L sample. The pitting potential shifted from 0.65 V to 1.1 V, a 74% improvement in corrosion response.

In order to enable evaluation of powder treatments, a method was needed to minimize the powder volume required. To produce the corrosion samples for the first part of the study, 20kg of powder was needed, which significantly limits the number of powder runs that can be reasonably accomplished. To circumvent this challenge, JHU/APL developed a technique to produce corrosion samples using less than 100g of powder. This method involves modifying the powder build volume in combination with custom sub-plates. The reduced build volume module and custom build plates are shown in Figure 11.



Figure 11: Minimizing required powder volumes using a modified reduced build volume

316L powder feedstock was doped with $\sim 0.1\text{wt}\%$ Ce, and SEM micrographs of the particles are shown in Figure 12. The coating provides a uniform distribution of the alloying elements which should minimize segregation during fabrication. Also, there is no measurable change in geometric size or shape to the feedstock powder, which potentially ensures that powder flowability and processability are not affected. The elements on the surface become incorporated into the build in the laser consolidation step. A sample that has been laser processed via SLM is shown in Figure 13. After processing, Ce can be detected in the 316L in the form of small sub-micron inclusions (Figure 13). This is a strong indicator that the Ce is well distributed and should provide the intended corrosion protection throughout a part.

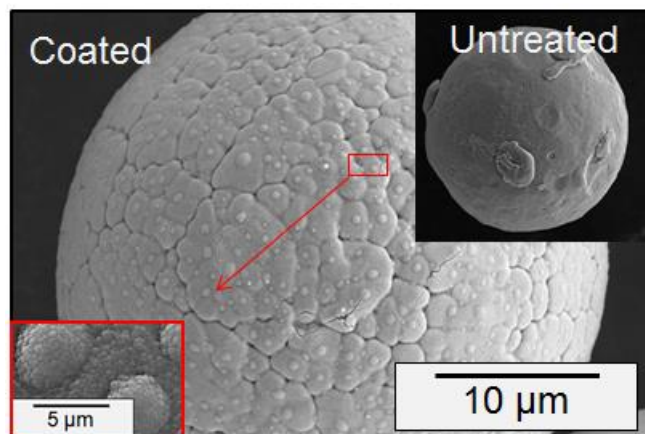


Figure 12: A powder particle shown both pre and post Ce-processing.



Figure 13: A corrosion test sample made from Ce-doped material.

The next challenge to tackle with respect to custom Ce dopants is the correct oxidation state. Ce^{3+} is needed to ensure passive corrosion inhibition on demand. Preliminary work on the feedstock modification indicates that the Ce is in the (4+) oxidative state. This is likely due to oxygen uptake, which is common in the AM process, due to surface oxidation of the AM feedstock. To improve the oxidation state of Ce in the AM solidified material, oxidation reduction reactions can be leveraged. A forming gas can be used to trap oxygen, which will reduce the Ce^{4+} to Ce^{3+} , thus enabling the ideal dopant state. Future work in oxide reduction reaction will be utilized to improve the on demand corrosion inhibitor technique.

Conclusions

Significant progress was made toward understanding the mechanisms of corrosion in AM 316L during this one year effort. The primary objective was to improve corrosion resistance in Additively Manufactured (AM) 316L Stainless Steel. To achieve this objective, we utilized a dual approach of feedstock modification and optimized processing parameters. Surface modified feedstock powders were produced to enable custom alloys tailored for corrosion performance. These were subsequently processed with selective laser melting, resulting in uniform dispersion of Ce throughout the AM parts, which was demonstrated via EDS chemical analysis. Initial surface treatments resulted in a nearly doubled corrosion potential, indicating the promise of Ce treatments.

In addition to material modification, effects of processing parameters have been elucidated to enable fundamental control over the solidification behavior of unmodified AM 316L. Reduced laser speed was shown to be critically linked to improved pitting corrosion and a reduction in grain boundary attack, as determined using a newly developed method to evaluate the pitting performance.

Future Work

Opportunities for future work have been unveiled over the course of the past year. With respect to custom material modification, revolutionary gains in corrosion performance are possible with only minor adjustments to the alloy's chemistry. The use of oxide reduction reactions to convert Ce^{4+} to Ce^{3+} will maximize the passive corrosion inhibiting form of Ce. This can be completed via hydrogen + argon shielding gasses (forming gas) while manufacturing in the SLM system. In addition to Ce, other dopants such as SiC have the potential to improve crevice and sensitization

problems. SiC dopants can help to stabilize pH at crevice prone locations while simultaneously optimizing solidification behavior by eliminating the formation of chrome carbides at grain boundaries and thereby eradicating the sensitization problems. In parallel, processing parameters can be tuned to minimize sensitization, in a collaborative effort with the Kelly group at UVA. By adjusting the solidification rates, chrome carbides can be dissolved at the time of formation, thus eliminating the problem with grain boundary sensitization. Finally, the impact of laser solidification mechanics can be studied using small electrochemical cells to enable direct quantification of the impact of meltpool and grain boundaries on corrosion performance of AM 316L. The work performed during this first year study lays the groundwork for several interesting investigations in the future which can fully elucidate AM 316L corrosion mechanisms and, importantly, identify methods to reduce its corrosion.

References

- [1] Thijs, L., et al., "Fine-structured aluminium products with controllable texture by selective laser melting of pre-alloyed AlSi10Mg powder," *Acta Materialia*, Vol. 61, No. 5, 2013, pp. 1809-1819.
- [2] Liu, Y., et al., "Gradient in microstructure and mechanical property of selective laser melted AlSi10Mg," *Journal of Alloys and Compounds*, Vol. 735, 2018, pp. 1414-1421.
- [3] Read, N., et al., "Selective laser melting of AlSi10Mg alloy: Process optimization and mechanical properties development," *Materials & Design*, Vol. 65, 2015, pp. 417-424.
- [4] Olakanmi, E.O.t., R. Cochrane, and K. Dalgarno, "A review on selective laser sintering/melting (SLS/SLM) of aluminium alloy powders: Processing, microstructure, and properties," *Progress in Materials Science*, Vol. 74, 2015, pp. 401-477.
- [5] Liu, A., C.K. Chua, and K.F. Leong. "Properties of test coupons fabricated by selective laser melting," *Key Engineering Materials*. 2010.
- [6] Buchmayr, B., et al., "Laser Powder Bed Fusion—Materials Issues and Optimized Processing Parameters for Tool steels, AlSiMg- and CuCrZr-Alloys," *Advanced Engineering Materials*, Vol. 19, No. 4, 2017.
- [7] Aboulkhair, N.T., et al., "On the formation of AlSi10Mg single tracks and layers in selective laser melting: Microstructure and nano-mechanical properties," *Journal of Materials Processing Technology*, Vol. 230, 2016, pp. 88-98.
- [8] Leary, M., et al., "Selective laser melting (SLM) of AlSi12Mg lattice structures," *Materials & Design*, Vol. 98, 2016, pp. 344-357.
- [9] ASTM G61-86(2018) Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys, ASTM International, West Conshohocken, PA, 2018,
- [10] Sander, G., et al. "On the corrosion and metastable pitting characteristics of 316L stainless steel produced by selective laser melting." *Journal of The Electrochemical Society* 164.6 (2017): C250-C257.
- [11] Macatangay, D. A., et al. "Unexpected Interface Corrosion and Sensitization Susceptibility in Additively Manufactured Austenitic Stainless Steel." *Corrosion* 74.2 (2017): 153-157.