Corrosion of Additively Manufactured Stainless Steels—Process, Structure, Performance: A Review

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The corrosion of additively manufactured (AM) metallic materials, such as stainless steels (SS), is a critical factor for their qualification and reliable use. This review assesses the emerging knowledgebase of powder-based laser AM SS corrosion and environmentally assisted cracking (EAC). The origins of AM-unique material features and their hierarchical impact on corrosion and EAC are addressed relative to conventionally processed SS. The effects of starting material, heat treatment, and surface finishing are substantively discussed. An assessment of the current status of AM corrosion research, scientific gaps, and research needs with greatest impact for AM SS advancement and qualification is provided.

KEY WORDS: directed energy deposition, heat treatment, martensitic, selective laser melting, stress corrosion cracking, 304 and 316 stainless steel

INTRODUCTION

Additive manufacturing (AM) has become desirable for manufacturing, complex, net-shape, and small batch metal parts across nearly every sector, from energy to medicine. Locally high cooling rates along with highly nonequilibrium and directional solidification conditions during these processes result in microstructures considerably different from their conventionally processed counterparts. Although the linkage between processing, microstructure, and mechanical properties of AM metals has received considerable attention, the corrosion performance of these materials has only recently been considered—a critical factor for their qualification and use in many service environments.

One of the most prevalent and widely researched AM alloy classes to date is laser powder fusion stainless steel (SS), with corrosive service applications ranging from nuclear reactors to naval ships. Laser powder bed selective laser melting (SLM), which is also referred to as laser powder bed fusion (LPBF), and laser directed energy deposition (DED) are the primary processes routes for AM stainless steels in industry and research. Herzog estimated in 2016 that nearly 90% of AM stainless steels in industry and research and development were processed using SLM, while DED accounted for 10%.[1] Although the ratio may have shifted toward SLM since this time, these two remain the dominant processing routes and will serve as the subject of this review.

Table 1 lists pre-alloyed commercially-available SS powders, highlighting those alloys that have received attention in the literature addressing corrosion of AM SS. Only a small handful of alloy compositions have been examined to date and there is ample room for development of new AM-specific alloys. It is clear from Figure 1, that austenitic stainless steels are the most well-studied, specifically Type 316L (UNS S31603[1]), which is reflective of its availability. It is also apparent in this figure that neutral chloride environments, as surrogates for seawater, body fluid, and other common natural environments, have received the greatest attention.

Research to date on AM alloys has revealed their corrosion and environmentally assisted cracking (EAC) performance, much like their mechanical performance, is influenced by a range of AM-unique microstructural and defect features across multiple length scales, from nanoscale nonmetallic inclusions to microscale porosity. The nature and distribution of these features can vary considerably within a single build and from build-to-build, dependent on a wide-ranging process and starting material parameter space. Defining the inter-relationships between process parameters, micro- and macrostructure, and corrosion performance poses a challenging prospect, which is only compounded by environmentally-specific behavior. For example, numerous studies of AM 316L in neutral chloride media have reported considerably higher pitting resistance compared to wrought 316L, while some studies have reported the opposite.[2,7] These conflicting findings are in part reflective of the highly variable material quality via starting material and process from study-to-study and the convoluted influence of a multiplicity of microstructural features (e.g., pores, inclusions) that are captured during bulk electrochemical measurement methods.

This review serves to provide a critical and deep dive into the corrosion and, where there is precedence, the EAC of LPBF...
Although there have been several vital general reviews and perspective papers over the last couple of years on the corrosion of AM metals, most provide only topical summaries for any particular alloy class.8-10 An in-depth review of AM SS is warranted given the relatively large and growing number of corrosion studies on the subject and the wealth of existing corrosion knowledge on powder metallurgy (PM), laser welding, and laser surface processing that can be leveraged to provide a deeper scientific understanding. This review does not address powder bed fusion electron beam melting (EBM). There are relatively few studies on additive EBM processing of SS. This is in part due to the need to preheat the powder bed during the build, which can lead to SS sensitization in the as-built component.11 Wire-feed processes are also outside the scope of this review, given the strong similarities of wire-feed AM SS to conventional autogenous multi-pass welds and the sparse corrosion studies on wire-feed AM SS.

The objective is to address the current state of understanding, gaps in scientific knowledge, and research needs with greatest impact for advancing the understanding of process—structure-performance for material advancement and technical basis for qualification in corrosive service environments. Where possible, we attempt to synthesize AM data and existing knowledge of SS corrosion to provide deeper insight on how the unique microstructures, surface morphology, and residual stress hierarchically govern observed corrosion resistance. The impact of starting material, processing, and postprocessing on performance are addressed, highlighting possible process and starting material pathways that could be used to create more corrosion resistant SS. Many of the topics and issues addressed are broadly applicable to other AM alloy classes and should be informative for researchers and practitioners interested in the corrosion of AM metallic materials.

### ADDITIVE MANUFACTURING PROCESS

Figure 2 schematically illustrates the SLM and DED processes and primary parameters that control the as-built material characteristics. SLM involves first spreading a thin layer of metal powder across a work area. A laser beam is then scanned across the powder bed to selectively fuse together a pattern in the layer via overlapping melt tracks. Another layer is then spread on top of the previous and the process is iteratively repeated to build up a three-dimensional part in a layer-by-layer fashion. DED is also a layer-by-layer process but differs from SLM in that the powder feedstock is blown out of one or numerous nozzles through the laser beam and into the melt pool on the substrate. A comparative summary of prototypical characteristics for each process is given in Table 2.

The key parameters given in Figure 2 and Table 2 characterize feedstock mass input (powder layer thickness and feed

Table 1. Commercially-Available Pre-Alloyed SS AM Powders

| Alloy Class | Alloy(A) |
|-------------|----------|
| Austenitic  | 218, 304L, 310S, 316L, 316Ti, 904L, Biodur 108 (UNS S29108) |
| Martensitic | 410L, 420, 440C, 440B, 17-4, 13-8, 15-5, Custom 465 (UNS S4650) |
| Duplex      | 329, 2507, 2205 |

(A) Bold indicates associated with AM corrosion studies.

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rate) and heat input for melting the substrate (laser power, focal beam diameter, and scan speed), which in turn govern the melt pool characteristics, including temperature and cooling rate. Build energy density is a reduced order parameter representative of heat input and commonly used to characterize both AM and conventional laser/welding processes:

\[ E = \frac{P}{d \cdot v} \]  

where \( P \) is laser power, \( d \) is focal beam diameter, and \( v \) is scan speed. This equation can be used to estimate melt pool and solidification characteristics. Higher energy densities (e.g., fast scan speed and low power) generally result in faster cooling rates for a given mass input. DED is generally a higher energy process than SLM with larger melt pools and slower cooling rates. More sophisticated energy density models have been proposed that include other process factors, such as hatch spacing and, for DED, powder feed rate.

The parameters controlling energy and mass input along with scan strategy fundamentally affect the underlying thermal gradient (\( G \)) at the solid/liquid interface and the solidification growth rate (\( R \)) of the interface bounding the moving melt pool. The ratio \( G/R \) controls the morphology of the solidification structure—planar, cellular, columnar, dendritic, and equiaxed dendritic in order of decreasing \( G/R \). The cooling rate \( G \times R \) determines the dimensions of the solidification structure. The fast cooling rates of DED and SLM generally produce finer microstructure than conventional thermal processing (e.g., solution annealing and water quenching, casting, arc welding). As-built DED microstructures, however, are generally coarser than SLM due in part to slower cooling rates and are often most comparable to conventional autogenous laser welds. There are numerous excellent and in-depth reviews that cover these matters in greater detail. Simple changes in energy density, mass input, scan pattern, and other more subtle parameters, such as feedstock morphology, can dramatically affect feature size, morphology, and texture. This will be further discussed in the sections that follow.

**MATERIAL STRUCTURE**

Characteristic features common to both DED and SLM processed components that have a known or expected effect on corrosion are given in Figure 3. The AM material

| Table 2. Typical Process Characteristics for SLM and DED |
|-----------------|-----------------|
| SLM             | DED             |
| Laser power (kW)| 0.1–1           | 1–5              |
| Focal laser beam| 0.001–1         | 0.1–5            |
| diameter (mm)   |                 |                  |
| Scan speed (mm/s)| 10–1,500        | 5–20             |
| Max powder feed | –               | 0.1–1.0          |
| rate (g/s)      |                 |                  |
| Layer thickness | 0.02–0.1        | 0.04–1           |
| (mm)            |                 |                  |
| Dimensional    | 0.04–2.0        | 0.5–1.0          |
| accuracy (mm)   |                 |                  |
| Build atmosphere| N₂, Ar          | N₂, Ar           |
| Cooling rate (K/s)| 10⁶–10⁷       | 10³–10⁶          |

*FIGURE 3.* (a) Composite 3D reconstruction of as-built SLM 316L material. Secondary electron (SE) images show the as-printed top and side surfaces (gray scale), optical micrographs of the polished and etched cross sections are shown in brown, and grain structure of the same electropolished material via electron backscatter diffraction (EBSD) is shown in green. Surrounding panels detail specific features: (b) EBSD map showing grain structure in relation to melt pools (dotted curves outline boundaries) with secondary electron inset detailing substructure and melt pool boundaries, (c) transmission electron microscopy (TEM) detail of substructure with high angle annular dark-field/electron dispersive x-ray spectroscopy (HAADF/EDS) inset showing Cr segregation and Si-rich oxides (black/blue circles), (d) lack of fusion void, and (e) gas pore.
superstructure is comprised of a series of melt pools organized in a periodic pattern reflective of the scan strategy, Figure 3(a). The microstructure is characteristically a mixture of fine scale equiaxed and columnar solidification grains along with cellular or cellular-dendritic substructure. As with multi-pass welding, columnar grains typically grow epitaxially from the previously deposited layer at the boundary of the melt pool. Grain growth direction is along the direction of maximum heat flow. The resultant microstructural heterogeneity can be visible as periodicity corresponding to layer height, hatch distance, and scan pattern used, Figures 3(a) and (b).19 Cellular solidification substructure with accompanying elemental microsegregation of alloying species is commonly present in both SLM and DED SS as a result of highly nonequilibrium cooling, Figure 3(c).15,18-19 The operative microsegregation is a function of alloy composition (thermodynamic) and process (kinetic) parameters. Dispersed secondary phase inclusions, such as oxides, are also common in these materials and at a much finer scale (nm compared to μm) than their conventionally processed counterparts.20 The bulk material contains nontrivial populations of process defects such as porosity (e.g., lack of fusion and gas), Figures 3(d) and (e), and, in some cases, solidification cracks.12 The as-built surface is even more defective and rough due to incomplete powder fusion and, in some cases, melt pool breakup (e.g., balling) during the build along with melt track waves, Figure 3(a).

There are several generalities regarding the phase constitution of AM SS microstructures in terms of process route, alloy type, and typical alloy compositions of commercially available AM SS powders. The rapid cooling operative in SLM processing (10^5 K/s to 10^6 K/s) of austenitic alloys (e.g., 304L [UNS S30403], 316L) is generally observed to produce fully austenitic microstructures via primary austenite solidification.15 This is largely due to the solidification growth rate and dendrite tip undercooling expected in SLM which is mechanistically similar to that reported for high energy density welds on stainless steel.31-32

The comparatively higher heat input DED process, due primarily to a slower cooling rate, Table 2, will often exhibit a solidification path that can be predicted from the alloy composition using weld constitution diagrams.25 Commercially available compositions of austenitic stainless steel powders that are processed via DED typically produce microstructures comprised of austenite with up to a few percent retained delta ferrite in the cellular substructure.16,18 This is a result of the primary ferrite solidification with incomplete solid state transformations from delta ferrite to austenite upon cooling; see the Texture section for further detail.

AM processing of other SS alloy classes can also cause phase constitution deviations relative to conventional processing routes. AM martensitic stainless steels can contain considerable amounts of retained austenite, which has been attributed to various factors including high residual stress imparted by high cooling rates, partitioning of austenite stabilizing elements during thermal cycling, or elevated nitrogen content inherent to the starting powder or build atmosphere.25-26 Papula and coworkers demonstrated that SLM processing of 2205 duplex alloy can produce near fully ferritic specimens (99 vol%) due to rapid cooling rate suppression of the solid-state austenite transformation.27 They found that postbuild annealing at 950°C for upward of 5 min produced the duplex structure.

In addition to principal phases, the fast cooling rates of DED and SLM processes also tend to suppress formation of intermetallics, such as carbides, sigma, and chi, along with nonmetallic phases (MnS) that are deleterious to corrosion resistance.15,27 The material and microstructural characteristics overviewed in this section will now be addressed in greater detail in terms of their relation to processing and impact on corrosion behavior.

### 3.1 Texture

Preferential crystallographic orientation is ubiquitous in powder-based AM fusion processes, resultant from epitaxial nucleation and competitive grain growth. Grains typically tend toward <100> orientation in the direction of the heat flow in the melt pool on previously deposited layers. This is seen in Figures 3(a) and (b). The nature and extent of texturing is dependent on factors affecting thermal gradient and solidification rate in the melt pool along with scan strategy (see the Additive Manufacturing section). For example, larger melt pools with inherently slower cooling rates promote texture due to enhanced coarsening and recrystallization in the heat affected zone, while smaller melt pools can lead to fine-grained weakly textured microstructures.1

Texture control via scan strategy is gaining interest in AM processing as means of controlling material properties, including corrosion.26-30 Recently, Sun and coworkers demonstrated SLM production of lamellar textured 316L with major lamellae of <011> grains and minor lamellae of <001> of grains aligned in the build direction.29 The authors reported breakdown potentials (E_{b}) near 1.2 V_{SCE} in 0.9 wt% NaCl at 37°C, claiming that the superior pitting resistance relative to conventional 316L (0.5 V_{SCE}) was imparted by the unique texture. Regardless of why such texture could improve pitting resistance, their study serves to exemplify the possibility of texture control in AM for corrosion purposes. Other recent studies have demonstrated creation of near single crystal structures via SLM, which could be advantageous for corrosion resistance.31

The role of texture on corrosion resistance in laser-processed SS has been explored in several laser surface melting (LSM) studies, but with conflicting findings.32-35 Close analysis of several of these studies suggests that reported trends in corrosion resistance as a function of texture, for example, were confounded by differences in distributions of δ-ferrite, nonmetallic inclusions, and grain boundary nature imparted by the different processing conditions used to achieve the textures.35 In other words, crystallographic texture can often be secondary to stronger corrosion-inducing features, which is important given the controlling role of defects in in the corrosion of AM SS as will be discussed later. In the absence of these strong features, however, Sharyari, et al., found that for high purity 304L in 1 M NaCl, grain orientations with the highest atomic density (e.g., [111] and [100]) were most resistant to pit initiation.36 Thus, provided strong pit initiation features could be minimized in AM SS, such as porosity and secondary phases, texture control could be advantageous for corrosion resistance. Texture engineering via AM may also be a route to mitigate EAC under certain environments.37-38

### 3.2 Solidification Substructure

Except for pure metal systems or conditions with large imposed undercooling, solidification microstructures formed exclusively by planar front solidification are not generally observed. Rather, cellular or dendritic structures are formed during solidification as a result of an instability or breakdown of a planar solid/liquid interface. As first proposed by Chalmers, such instability caused by constitutional supercooling is resultant from a solute-rich boundary layer in which the plane front...
protrudes outward into the liquid and results in the cellular and/or dendritic structures observed in solidification microstructures, including metal additive. Resultant AM solidification microstructures are readily apparent with microscopic examination when metallographically prepared and chemically etched, Figure 4. The redistribution of solute during solidification across cell and dendrites, Figure 3(c), produces a spatially heterogeneous reaction with the chemical etchant thus revealing structure. Solute redistribution depends on thermodynamic factors such as the SS alloy composition as well as pertinent kinetic factors, such as cooling rate, controlled by the AM process parameters. Studies performed over 30 y ago on the rapid solidification behavior of stainless steel welds, including partitioning behavior and solid state transformations, still serve as the technical foundation for interpreting microstructures in AM stainless steel.22,40-43

Another unique feature of AM SS solidification microstructures is the presence of a dislocation substructure that generally corresponds morphologically to the solidification microstructure (i.e., cellular or dendritic microstructure), Figure 4(b). These dislocation networks in SS have been reported by Lui, et al.,44 however, the presence of similar dislocation substructures was first reported in the technical literature for 316 SS (UNS S31600) arc welds as early as 1982 by Foulds.45-46 Dendrites in the weld metal corresponded to “subgrains” misoriented by less than 1° with dislocations accommodating the mismatch. This dislocation substructure, first discussed in austenitic SS welds, is mechanically like that observed in AM SS microstructure, albeit with relatively finer characteristic dimensions corresponding to the higher cooling rate.

The effect of solidification substructure on corrosion behavior is dependent on both substructure characteristics and the corrosive environment. In environments that promote passive behavior, such as neutral chloride or dilute acid environments, several investigators have postulated that subgrain boundaries in SLM austenitic SS serve to improve passive film characteristics in a manner like that proposed for nanocrystalline grain refinement of stainless steels.47-50 Specifically, the subgrain boundaries have been suggested to enhance passivity by providing a high density of preferential oxide nucleation sites that promote and enhance barrier characteristics.48 Lodhi, et al., for example, attributed the 10 times lower passive current densities measured during anodic potentiodynamic polarization on SLM versus wrought 316L in weak (<0.1 M) sulfuric acid (H₂SO₄) solutions to this substructure effect.47 Lower passive current density values and, in some cases, enhanced oxide impedance relative to wrought, have been reported in neutral chloride media.49-50 In other studies, however, these trends are either not apparent or the inverse relationship was reported.10,51 One possible reason for these mixed results is that electrochemical behavior measured using bulk methods (e.g., 1 cm² test areas) can convolute substructure electrochemical contributions with the effects of other microstructural features that can dominate response, such as pores.10,51 Differences in thickness and compositional profiles of the native oxide on SLM versus wrought 316L are not, in our opinion, readily apparent within the uncertainty of the analysis techniques used—glow discharge optical emission spectroscopy and x-ray photoelectron spectroscopy (XPS).49-50 Additional electrochemical data, such as repassivation kinetics, along with more detailed studies that examine material factors in isolation (e.g., residual stress, defects) would help to further elucidate the relationship between substructure and passivity.

Environments that promote active corrosion, such as highly oxidizing or acidic conditions, can cause selective attack of the substructure, dependent on the extent and nature of solute segregation. This is why these features are readily apparent during microscopic examination after metallurgical etching. For example, Saiedi, et al., reported preferential etching of solute (Cr, Mo) segregated SLM 316L cell interiors after exposure to 2% hydrofluoric acid (HF) and 8% nitric acid (HNO₃), Figure 4(a).52 Trelewicz, et al., postulated that the observed partitioning of Mo to the cell boundaries was responsible for the activation-controlled type dissolution of SLM 316L during anodic potentiodynamic polarization above open-circuit potential (OCP) in room temperature 0.1 M hydrochloric acid (HCl), but without direct evidence.53 It is very possible that other features, such as porosity, may have been responsible for this behavior instead. Others have reported selective attack of Cr, Mo depleted cell interiors within pits after anodic polarization in neutral chloride solution.10,54 Nakao and Nishimoto showed similar preferential attack of primary austenite-solidifying substructure for LSM 904L SS (UNS N08904) in ferric chloride.55-56

FIGURE 4. (a) Backscattered electron (BSE) image of etched SLM 316L substructure and (b) bright-field TEM image of dislocation structure at cell walls in SLM 316L. Reprinted with permission from Saiedi, et al.52
Furthermore, they demonstrated that the pitting resistance (pitting potential and critical pitting temperature) of this same material in ferric chloride solution increased with decreasing levels of microsegregation of Ni and Cr in the solidification substructure, Figure 5. The extent of solute segregation was controlled by changing scan speed during laser remelting.

While the rapid cooling rate of SLM often stabilizes single-phase, primary austenite solidification, the comparatively slower cooling rate of DED can result in different solidification behavior for commercially-available austenitic stainless steel powder. Primary ferrite solidification with retained intracellular/intradendritic δ-ferrite has been observed to have a considerable impact on the corrosion resistance of DED 304L and 316L. Figure 6. Melia, et al., showed that selective attack at intradendritic δ in 304L in 0.6 M NaCl controlled breakdown resistance of DED 304L. The breakdown potential of material produced with 0.45 kJ/mm heat input (10^3 K/s cooling rate) was an average of 100 mV lower than that produced with 0.03 kJ/mm (10^4 K/s). The lower breakdown potential for the higher power material was attributed to smaller/less δ and greater solute segregation at δ/γ interfaces. Also, unlike SLM 304L and 316L, the breakdown potential of the DED 304L was comparable to the wrought. The authors proposed that the any beneficial effect of reduction of nonmetallic inclusion size on breakdown potential, as seen in SLM (Nonmetallic Inclusions, section 3.4), relative to wrought was likely counteracted by susceptibility induced by δ and solute segregation. Zeitala reported lower breakdown potential of DED 316L versus wrought, also attributing the difference to the presence of δ and solute segregation.5

These initial studies combined with those on autogenous laser fusion welds and laser surface melting, with similar microstructures, evidence larger and more numerous δ features accompanied by chemical microsegregation at the δ/γ interface can decrease corrosion resistance of austenitic SS. These trends break down, however, when considering the large amount ferrite (e.g., 50%) in duplex SS which has a high δ-ferrite with elevated Cr and Ni content and solute segregation. A holistic understanding of how the amount and distribution delta along with nature of δ/γ interfaces affects corrosion behavior is lacking. Nonetheless, results to date suggest that for austenitic SS, corrosion resistance in environments that promote active corrosion might be enhanced by targeting higher solidification rates, compositions that inhibit segregation, or heat treatment.

The unique solidification structure of AM SS can also have considerable impact on its EAC behavior. Although studies directly examining the role of these features on EAC are few, a recent study by Kong, et al., reported that SLM 316L had superior resistance to hydrogen damage (i.e., martensite transformation) relative to its wrought counterpart. They attributed this to dislocation substructure providing high formation stress for martensite transformation. Under irradiation conditions, Song, et al., found that solutionized 316L had better radiation tolerance and lower irradiation-assisted stress corrosion cracking (SCC) susceptibility than stress relieved 316L (650°C for 2 h) due to instability of the residual dislocation substructure in the stress-relieved material.

### 3.3 | Melt Pool Boundaries

Melt pools boundaries (MPBs) are delineated by differences in grain or subgrain orientation, size, and morphology, Figures 3(a) and (b). These differences originate from the interplay between epitaxial growth and solidification rate and thermal gradients in the melt pool along with coarsening in the heat affected zone. Lack of fusion pores can also result along MPBs if track spacing is too wide for sufficient overlap. Some evidence has been presented that suggests MPBs could exhibit nonuniform residual stress distributions and possibly chemical segregation, but detailed information on these characteristics is lacking. Their unique nature, however, is obvious in that melt pool

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**FIGURE 5.** Relationship between the pitting potential and the amount of Cr and Mo (pitting index) measured in dendrite cores of LSM SS 904L solidification substructure. The relationship between core composition and scan speed (v) during laser remelting is indicated by the arrow. Adapted from Nakao and Nishimoto.
boundaries are selectively attacked by oxidizing, acidic media, such as etchants, which make them clearly visible.

Studies to date indicate that MPBs could play an important role in corrosion, especially in the case of highly oxidizing, acidic conditions, including crevice-type environments. Selective attack of melt pool boundaries has been reported in both SS sensitization tests and during anodic polarization in chloride media. Macantangy, et al., found that trenching of MPBs in SLM 316L resulted from persulfate etching following a standard sensitization test. They surmised, based on x-ray diffraction (XRD) analysis and etching behavior after annealing, that the trenching was likely not due to chromium carbide precipitation. They speculated that it may be related to sigma phase or chromium nitride formation during the build and that more detailed analysis of MPBs was necessary. Others have reported similar selective trenching of SLM 316L MPBs by oxalic acid etchant or FeCl₃ (ASTM G48). Figure 7. Additionally, Zhou, et al., reported that pitting preferentially occurred at MPBs during anodic polarization in 3.5 wt% NaCl. They speculated that MPB attack was due to inhomogeneous microstructure, pores, residual stress, and unstable nonmetallic elements in the MPB but without definitive evidence. Further clarification of the origin of MPB selective attack and its role in localized corrosion and EAC is critically important for understanding the reliability of AM SS.

3.4 | Nonmetallic Inclusions

The nature and distribution of nonmetallic inclusions in powder-based AM SS, such as oxides and sulfides, differ in composition, size, and shape considerably from their conventional, thermomechanically processed counterparts. Figure 8 exemplifies the inclusion characteristics of AM and conventional wrought stainless steel. As seen in this figure, inclusions of conventional commercial purity alloys are usually on the order of 1 µm to 10 µm in size and can vary in shape, dependent on processing route (e.g., spherical, polyhedral, stringer). Mn-rich sulfide and Al, Mg, Mn, Si, Ca, Cr oxide inclusions are most common in conventionally produced SS and are known to act as preferential pit initiation sites. The relatively fast solidification rates of DED and SLM processing suppress growth and produce finely distributed spherical Si- and Mn-rich oxide inclusions, typically <1 µm diameter for a wide range of alloys. Such inclusions are morphologically similar to those found in welds, albeit considerably smaller due to the high cooling rates of AM, Table 2. Numerous studies on LSM and high-purity stainless steel have established a strong correlation between smaller MnS-rich inclusions in as-built components and the higher pitting potential in neutral chloride media. McCafferty and Moore were some of the first to show that laser surface melting of austenitic SS can enhance pitting resistance, increasing the pitting potential (Epit) of wrought 304 by at least 200 mV in 0.1 M NaCl. McCafferty and Moore attributed this to scale down of MnS inclusions. Several investigators since have reported that below ~1 µm characteristic size, individual sulfide inclusions are too small to promote nucleation and growth of pits in neutral chloride media.

Like the LSM studies, several studies have demonstrated significantly higher pitting potentials of austenitic AM SS in chloride solutions relative to conventional material (oftentimes hundreds of mV), which is attributed to scale down of oxides and amplification of MnS-rich inclusions. Oxide inclusions in conventional SS can serve as weaker preferential pitting sites of SS in some environments but are possibly too small in AM SS to support pitting. The superior pitting resistance of
austenitic SS devoid of approximately >1 μm MnS inclusions, but still containing oxide inclusions, evidences their weak role in dilute neutral chloride solutions. Under more aggressive conditions, however, several studies have shown that preferential pit initiation and growth at the oxide/matrix boundary for inclusions in conventionally processed 304 or 316L under aggressive conditions, such as concentrated, elevated temperature, acidic, or oxidizing chloride solutions. Other studies have reported no preferential attack of oxides under similarly aggressive conditions. Few investigators have directly examined the role of oxides on the pitting behavior of AM SS. Schaller, et al., found pitting potentials of SLM 304L in NaCl solutions (up to 1 M) hundreds of mV higher than high-purity wrought 304L which lacked MnS inclusions observable by SEM/EDS. This was despite the SLM material being 0.3% porous, which can be detrimental to pitting potential as will be discussed in the Bulk Defects section. In the absence of detectable MnS in the wrought material, the authors proposed that the superior pitting resistance was due to the much finer oxide inclusions of the SLM material compared to the wrought (5 nm to 20 nm vs. 2 μm to 4 μm diameter, respectively). Melia, et al., found the pitting potential of DED 304L (40 wt ppm to 60 wt ppm S) in 0.6 M NaCl similar to that of nonresulfurized (<10 wt ppm S) wrought 304L with no observable MnS. They proposed that the presence of considerable delta ferrite in the DED material (~2 vol%) controlled breakdown potential and likely counteracted any beneficial effect of oxide inclusion scaling. They also examined pitting attack locations on the polished DED samples after short anodic holds and found in most cases attack was associated with delta ferrite in the material. They reported that in rare instances pitting initiated at the oxides. A comparison of attack morphology seen in their work compared to attack observed of larger oxide inclusions in conventionally processed material is seen in Figure 9.

One explanation for the scaling effect of oxides derived from the results of these studies is that the spherical nature and size of AM oxides are not conducive to setting up conditions for pit propagation. Pits growing around nanoscale inclusions may quickly undercut them before becoming large enough to transition to stable pits, negating any beneficial effect of occluding chemistry, Figure 9. Despite the apparent beneficial effect of annihilation or scale down of inclusions, and given the ubiquity of oxides in AM metallic materials, there is a need for better mechanistic understanding of the scaling effect of nonmetallic inclusion size, shape, and chemical nature on corrosion behavior within the context of powder-based AM. This is especially important given the inclusion precipitation and coarsening behavior that has been reported after solution annealing treatments (see Heat Treatment, section 5.1).

Nonmetallic inclusions are known to considerably affect the EAC behavior of conventionally processed SS in certain environments but have received little attention for AM metals. An initial study on SCC of SLM 316L by Lou, et al., reported that Si-rich oxides along grain boundaries preferentially dissolved and appeared to facilitate crack growth and promote crack branching in high-temperature water. Similar detrimental effects of inclusion dissolution on both crack nucleation and growth in SCC in high-temperature water have also been reported for conventionally processed 316L. Additionally, dependent on shape, size, and distribution, inclusions may serve as hydrogen sinks or facilitate hydrogen entry, increasing susceptibility to hydrogen embrittlement. On the other hand, the improved pitting resistance of some SLM SS imparted by scale down or annihilation of inclusions may also suppress crack nucleation in saline environments. The role of inclusions in corrosion fatigue is another critically unaddressed knowledge gap, as several studies have demonstrated the finely dispersed oxides in powder-based AM can reduce impact toughness, ductility, and fatigue life by serving as crack nucleation sites.

### 3.5 Bulk Defects

Lack of fusion voids, pores, and cracks are the most common defects in AM metals and can adversely affect corrosion behavior. Typical characteristics of these defects and their processing origins are given in Table 3. Lack of fusion (LOF) voids are typically tortuous, can contain sharp edges, propagate through multiple melt pools, and contain partially melted powder particles, as seen in Figure 10. By contrast, gas pores are typically ellipsoidal in nature, although some pores formed from keyhole collapse may be irregularly shaped.

The irregular geometry of LOF voids may provide crevice-type occluded areas that promote the development of aggressive corrosion chemistry and IR drop, with considerable detriment to corrosion resistance. Several studies have shown that LOF voids can serve as strong preferential sites for corrosion attack and control the breakdown potential to the first order. Schaller, et al., reported that the active corrosion of SLM 17-4 PH (H900 condition) in room temperature...
0.6 M NaCl was exclusively due to crevice corrosion occurring within the LOF voids, Figure 11.101 They further demonstrated that by excluding lack of fusion pores, the pitting resistance of the material could be restored to that similar of wrought H900 17-4 PH. Melia, et al., showed that the presence of even one LOF void in DED 304L could reduce $E_p$ by 400 mV relative to LOF-free areas.18 Although geometry is likely the primary contributor to LOF preferential attack, the microstructure and chemistry of the pore-free surface may also play a role. For example, Melia, et al., reported larger δ-ferrite substructure near the surface of some LOF pores in DED 304L, which could impact pit initiation and repassivation.

Ellipsoidal gas pores may also promote localized corrosion, especially those that are partially covered as seen in Figure 10(b), but studies to date suggest they may play a lesser role relative to the more tortuous LOF voids.18-19,102-105 Duan, et al., demonstrated that pits can initiate and stably grow from partially covered gas pores during anodic polarization of SLM

| Defect Type    | Shape                                      | Size (μm) | Origin                                                                 | Process Factors                                                                 |
|----------------|--------------------------------------------|-----------|------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Lack of fusion void | Irregular                                   | 10–100    | Inadequate overlap and penetration of melt pool into previously deposited layer | Scan pattern, power density, powder packing, feedstock                         |
| Gas pore       | Spherical, ellipsoidal, irregular (keyhole) | 1–100     | Entrapment of melt pool vapors and build atmosphere; incorporation of gas from feedstock powder | Powder density, chamber environment, feedstock; scan pattern, power density     |
| Crack          | Curvilinear, branched                       | Any       | Stress between solidified and contracting solidifying areas of melt pool | Power density, melt pool thermal gradient                                       |

FIGURE 10. (a) Secondary electron image of lack of fusion void and gas pores in SLM 316L and schematic illustrative cross sections of (b) a lack of fusion pore and (c) a gas pore.

FIGURE 11. (a) Corrosion product buildup over a lack of fusion pore in SLM 17-4 PH after 7 d immersion in quiescent 0.6 M NaCl and (b) anodic polarization behavior of the same material in 0.6 M NaCl using a microelectrochemical cell over areas with (>50 μm) and without (<10 μm) lack of fusion pores compared to wrought 17-4 PH. Reprinted from Schaller, et al.101
Suryawanshi, et al.,90 where breakdown potential (Eb) considered no clear trends in corrosion behavior with porosity, as exemplified in Figure 12. In Figure 12 there are some cases, such as Suryawanshi, et al.,90 where breakdown potential (Eb) considerably increases with porosity. In other cases, such as Sander, et al.,4 there is no clear trend. The discrepancies in these trends likely stem from the strong dependence of pore and void size, morphology, and distribution on build parameters and feedstock characteristics, which is not captured by the porosity metric. How pores are exposed at the surface during corrosion testing (e.g., cross-section geometry), level of polishing, and the presence of residual debris in the pores are also possible contributors. Similar discrepancies between porosity and corrosion resistance have been reported for PM SS and attributed to varying pore characteristics across parameter space.108 Better understanding of the influence of processing conditions and starting material on pore and void morphology and distribution and, in turn, the causal linkage between corrosion susceptibility and these factors would help in qualification of processing parameters and parts.

The effect of defects on the EAC behavior of AM metals remains relatively unclear. Lou, et al., reported that SCC growth rates in solution annealed SLM 316L with 0.3% porosity was an order of magnitude higher than hot isostatic pressed (HIP) and solution annealed SLM 316L with 0.08% porosity in high-temperature water.109 This suggests that an increase in porosity in SLM 316L may enhance crack growth rate in high-temperature water. Aside from serving to promote crack initiation, it is possible that certain voids or pores could serve to effectively blunt the crack tip.

3.6 Printed Surface Defects

Surface quality tends to be a major drawback of AM parts, particularly for corrosive applications, with powder-based processes typically producing rough and highly defective surfaces. Although, post-build finishing can be used to tailor surface characteristics, as is discussed in Surface Finishing, section 5.3, there are many cases where the as-fabricated surface is desired, especially for net shape applications. Furthermore, for complex parts with internal surfaces, such as lattice structures, conventional surface finishing is either prohibitively expensive or ineffective.

There are several types of surface defects with potential impact on corrosion, including balling, partially fused powder particles, and staircasing. Balling is the formation of solidified droplets along the melt track resultant from melt pool breakup via Rayleigh instability.110 Staircasing is characterized by step-like features caused by the approximation of inclined surfaces (e.g., curvature) on a layer by layer basis.110 The nature and distribution of these features within a single build are largely dependent on the surface angle with respect to the build direction (inclination angle), as shown in Figure 13. The amount of partially fused powder particles and voids and, hence, surface roughness increases with inclination angle.111 Underhanging (downskin) surfaces typically having the greatest amount. The corrugated melt track pattern is most apparent at low angles, such as the relatively smooth top surface where powder particles are minimal. These differences are also reflected in the cross sections seen in Figure 13 with varying degrees of roughness and crevice-type features. Partially fused particles can also retain original microstructure, as seen in inverse pole figure maps. Defects are especially prominent for smaller, high curvature features, such as fine lattice struts. DED surfaces share some of the same characteristics but generally have higher amplitude corrugations and rougher surfaces (Rq > 10 μm) than SLM due in part to the larger melt pool.112-113 The few corrosion studies that have directly examined as-built AM surfaces have found severely diminished resistance relative to conventionally processed material and attributed this to the crevice-like geometry of surface porosity.114-116 A recent study by Melia, et al., found that the average breakdown potentials of SLM 316L as-built surfaces were at least 400 mV lower than a polished surface of the same material in 0.6 M NaCl.116 Furthermore, Eb varied widely with surface inclination angle with the rough downskin surfaces averaging 550 mV lower than the best performing and smooth upskin surfaces, Figure 14. Inclination angle dependence was attributed to the relative amounts and nature of the crevice-like porosity, as exemplified in Figure 13. The role of microstructural features associated with the partially fused powder, including retained powder microstructure and surface oxides, along with highly localized residual stress have remained unexamined but could also be a contributing factor to

![Graph](https://example.com/graph.png)
the behavior of an as-built surface. Another unexplored area for stainless steels is the effect of the as-built surface on EAC, which has been shown to be detrimental in other AM alloys.115

There are several potential avenues for reducing the impact of defects on the corrosion and EAC resistance, including feedstock, process, and alloy composition. Surface roughness is typically a strong function of partially fused powder particles, occurring with starting powder size, Figure 15(a). Increasing heat input can also decrease surface roughness, Figure 15(b). In-process surface finishing, via contour scan strategies, is another possible strategy for decreasing roughness. Laser remelting during the SLM build has been demonstrated to

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**FIGURE 13.** Surface characteristics of SLM 316L as a function of build inclination angle. Shown center is an as-printed parallelepiped prism. The topography of different faces is exemplified in the SE plan-view images and associated BSE micrographs (grayscale) and EBSD inverse pole figure maps (color) of cross sections through these surfaces. The top edge length of the prism shown in center is 15 mm. Additional material details are given in Melia, et al.116

**FIGURE 14.** (a) Anodic polarization behavior and (b) breakdown potentials of different SLM 316L as-printed surface orientations, a mechanically ground SLM 316L surface, and wrought 316L. The SLM material used is depicted in Figure 13. Adapted from Melia, et al.116
considerably reduce porosity and improve surface quality of top surfaces. This strategy involves rescanning the laser over the fused pattern, thus remelting it, before adding the next layer of powder. Yasa, et al., demonstrated reduction in bulk porosity in SLM 316L from 0.8 vol% to 0.03 vol% and a 90% reduction in $R_a$ on top surfaces (from 15 μm to 3 μm $R_a$). Although apparently effective, remelting during the build comes at the expense of production time. Furthermore, it is unclear how effective this strategy would be on inclined or downskin surfaces where the melt pool always borders the unfused powder bed.

Another means of mitigating the negative effects of surface and bulk defects is to utilize more corrosion-resistant alloy compositions. Alloys with elevated concentrations of Cr, Mo, and N (e.g., 904L), as indicated by the pitting resistance equivalent number (PREN) index, are generally more resistant to crevice corrosion. Copper and tin additions to austenitic SS can increase passivity and pitting resistance in certain environments, such as sulfuric acid. SS 304LSC and 316LSC are alloys of this type that are commercially utilized for powder metallurgy part production.

### 3.7 | Residual Stress

Laser-based fusion processes inherently introduce residual stresses into built parts that can approach or exceed the nominal yield strength of the material. Stress is induced by the high thermal gradients around the laser beam, rapid cooling, and the building up of successive layers whereby stress relaxation is mechanically constrained by the underlying the material. Residual stresses are a critical issue for manufactured parts as they can result in net shape distortion, detachment from the support structure, and cracking or failure of the AM part. Residual stresses are also known to impact passivity and EAC susceptibility of AM parts.

Residual stresses in AM parts are spatially nonuniform and dependent on part geometry and process, but there are notable characteristic trends in this regard. Residual stresses tend to be compressive near the core of a part and tensile near the surfaces. Of interest regarding corrosion test coupons, residual stress is typically greatest along the build direction for simple rectangular prism shaped parts after removal from the baseplate, such as plates and pillars. Residual stress distribution for an as-built SLM 316L part is shown in Figure 16, which exemplifies some of these trends. Several regions exceeding the nominal yield strength of annealed wrought 316L (200 MPa to 400 MPa) are apparent. Residual stresses can impact the corrosion resistance of AM components and should be considered during part design, build, and qualification. Externally applied compressive stresses are generally understood to be beneficial to corrosion resistance while tensile stresses, particularly at levels that induce plastic strain, have been shown to promote corrosion. Chao, et al., attributed the consistently higher pitting potential of as-built SLM 316L over stress-relieved material in 0.6 M NaCl to differences in compressive residual stress (~250 MPa versus ~25 MPa). A more recent study from the same group found that stress relief annealing of as-built...
SLM 316L resulted in decreased pitting potential, and increased passive current density and oxide donor density, specifically at 1,100°C for 5 min. They attributed this behavior to a decrease in residual compressive stress. It is possible, in our opinion, that thermally-induced microstructural change (e.g., inclusion precipitation) may have also been contributing factors, as discussed in Heat Treatment, section 5.1. In contrast to these studies, Sander, et al., recently reported no significant difference in pitting potential of as-built SLM 316L in 0.6 M NaCl between areas under tensile and compressive stress (180 MPa to -150 MPa).

Residual stress gradients in as-built AM parts should be considered in terms of EAC susceptibility, especially considering that tensile stresses typically occur on the exterior of parts and can exceed nominal material yield strength. DeBruycker reported severe cracking (multiple mm-sized cracks) of an as-built SLM 316L turbine part after 3 h in a boiling magnesium chloride solution, Figure 17. Stress relieving the parts for 2 h at 450°C minimized crack frequency. Annealing at 2 h at 950°C, which provided the greatest stress relief, eliminated cracks even after 78 h immersion. Additional studies on this topic are lacking in the literature, but the need to understand and account for the effects of residual stress at both the part-level and microstructural scale is clear. As with conventionally processed SS, the ASTM G36 boiling magnesium chloride test should be considered as a means of testing chloride-induced SCC susceptibility.

Process control strategies that address thermal gradients, and thus residual stress, during AM include scanning strategy, laser power, scan speed, build plate characteristics, and bulk powder/part temperature. To date several multiphysics finite element analysis (FEA) research-level and commercial AM software packages provide the capability for predicting macroscopic residual build stresses. These combined with knowledge of material-environmental conditions and environmental cracking behavior of the AM material could be used to determine the propensity and effect of EAC on a given component design.

POWDER FEEDSTOCK

The characteristics of SLM and DED processed materials and their properties are strongly influenced by the quality of the feedstock powder, which, to the first order, is determined by the powder production process. Gas atomization (GA) is the major process route for commercial stainless steel powder wherein a molten alloy is atomized by high-pressure flow of argon or nitrogen gas. GA powder particles are characteristically spherical and dimpled with some amount of roughness imparted by smaller satellite particles on their surface, Figure 18(a). Shape and size distributions can vary across manufacturers and lots and affect powder packing density (SLM) and nozzle flowability (DED) during the build process. This in turn contributes to porosity and surface roughness of the part and, hence, corrosion resistance. Furthermore, GA powders characteristically contain porosity formed by entrapped atomization gas which can translate into gas porosity in the consolidated SLM or DED material, Figure 18(b). The relationship between these defects and corrosion behavior are discussed in Bulk Defects and Printed Surface Defects, sections 3.5 and 3.6.

Nitrogen gas atomization can lead to nitrogen enrichment of SS powder with considerable effect on the AM material. For example, previous studies have shown that nitrogen atomized SS can contain up to five times the nitrogen content of Ar-atomized feedstock and conventionally processed material. At these levels, the elevated nitrogen suppresses martensite and promotes austenite leading to undesirable mechanical and corrosion properties.

The elevated oxygen content of the powder feedstock (from surface oxides and inclusions) combined with the build atmosphere can result in up to 10 times higher oxygen content of the AM consolidated material relative to conventionally processed alloys. Most of the oxygen in the consolidated material manifests itself in the oxide inclusions, discussed in Nonmetallic Inclusions, section 3.4.

Build quality is also dependent on powder storage, handling, and recycling procedures. Surface impurities from storage or handling conditions, such as sorbed water vapor, can promote powder agglomeration, degrade powder flowability/packability, and can lead to increased porosity in some cases. Deng, et al., showed that the bulk oxygen content of a build increased with humidified powders at well the size and volume fraction of inclusions. Given only up to 50% of the powder is consolidated into a part during typical SLM builds, powder is usually recycled for reasons of economy. As with powder storage, how powder degrades during reuse and how the degradation affects the properties of an AM part has received limited attention. Heiden, et al., found that particle size, particle roughness, and oxygen content of 316L powder increased after reusing it for 30 consecutive SLM builds. This correlated to lower density (high porosity) of parts built from the reused powder (97.7% versus 98.7% density from virgin powder) with only minor to no changes in the as-built part.

Additional studies explicitly addressing the role of powder quality and characteristics on corrosion performance of AM parts are lacking. This knowledge gap is nonetheless important to address for qualification of parts in corrosive service environments. Furthermore, the probable influence of powder quality on corrosion behavior could be better assessed if powder characteristics (e.g., atomization gas, reuse) were presented and addressed in more studies addressing corrosion of AM metallic materials.

FIGURE 17. (a) and (b) Optical micrographs of transgranular SCC in an as-built SLM 316L part after 3 h immersion in boiling magnesium chloride solution. The outer part surface is seen at the top of (a), including a partially fused powder particle. Reprinted from De Bruycker, et al.
5.1 | Heat Treatment

Post-build heat treatment is widely used to relieve residual stress, tailor mechanical properties, and homogenize microstructure. The thermal stability and evolution of AM SS microstructures is considerably different from conventional thermomechanically processed counterparts due to differences in starting microstructure and stored strain energy. Most AM SS annealing studies to date, including corrosion studies, have focused on SLM 316L and DED 304L, although duplex and martensitic stainless steels have also received attention.27,51,129,140-142 Given the solution annealing associated with 17-4 and 15-5 PH largely wipes out the as-built microstructure, save for porosity and nonmetallic inclusions, and that there are only a few studies to date on heat treatment of these AM-processed alloys, our attention will be focused here on austenitic SS.

Figures 19 and 20 illustrate the prototypical annealing characteristics of SLM 316L. Low-temperature annealing (600°C to 650°C) generally diminishes the cell dislocation structure, resulting in some amount of stress relief, Figure 20.129,142 At higher temperatures (~900°C to 1,100°C) and for periods of as little as 5 min, the solidification substructure can be largely annihilated, Figure 20(c), accompanied by grain growth that is influenced by melt pool shape, Figure 19(c).129,142-144 Melt pool boundaries also diminish, as seen in Figure 19(c).51,129 Recrystallization and grain growth dominate at higher solution annealing temperatures (1,100°C to 1,200°C), evolving toward equiaxed grains with characteristic annealing twins, Figure 19(d). Recrystallization can effectively erase as-built AM microstructure features, save for nonmetallic inclusions and porosity.143 It is notable that the recrystallization temperature of AM SS can be several hundred degrees higher than conventional cold-worked steel, due to the relatively low energy stored in AM versus the cold-worked material.145 Considerable amounts of oxides and Mn-S-rich nanoscale particles have been reported to precipitate at solution annealing temperatures.146

Several studies have found that high-temperature annealing (>1,100°C) can considerably decrease the corrosion resistance of SLM 316L in neutral chloride media.2,129,146-147 Comparing as-built and high-temperature stress-relieved (1,100°C for 5 min) SLM 316L, Chao, et al., reported comparable anodic polarization behavior but consistently lower pitting potential of the annealed material (0.56 V_{SCFE} vs. 0.74 V_{SCFE}).12 In the absence of solidification substructure and detectable secondary phases, the authors attributed the lower pitting potential to relief of compressive residual stress during annealing (~90% stress relief of original 248 MPa). Similar decreases in pitting potential have been reported by others along with, in some cases, increases in passive current density.129,146-147 The origin of this behavior has been attributed to a multitude of observed microstructural changes, including melt pool boundary dissolution,147 substructure annihilation,12 and precipitation of nonmetallic inclusions. Regarding the latter, a recent study by Laleh, et al., shows a convincingly strong correlation between the appearance of oxide and Mn-S precipitates and the depression of the pitting potential, which could well explain the trends observed by others.146

Figure 21 from this study shows a 300 mV drop in average pitting potential in 0.6 M NaCl between annealing SLM 316L at 900°C and 1,200°C.
1,000°C and 1,100°C. The authors found that the number of precipitates also increased with time, which may explain the slightly lower average value at 1,200°C for 60 min and the decreasing pitting potentials with time reported by Kong.\textsuperscript{147} Figure 22. Based on results to date, high-temperature heat treatment should be carefully considered for application of SLM 316L in neutral chloride environments. In other environments, high-temperature annealing may be beneficial. For example, Kong, et al., found annealing at 1,050°C for 30 min to considerably decrease SLM 316L passive current density in a highly acidic fuel cell environment, possibly due to dissolution of acid-susceptible substructure and melt pool boundaries.\textsuperscript{148}

The effect of lower temperature stress relief annealing on the corrosion of SLM 316L is less clear, although it appears that annealing at 600°C to 700°C may cause sensitization but to possibly a lesser degree than conventional wrought material. Cruz, et al., examined SLM 316L at 400°C for 4 h and 650°C for 2 h in 0.5 M NaCl, but it is not clear from the results presented that there is significant difference from the as-built material in pitting potential, passive current density, or impedance.\textsuperscript{129} The authors also did not observe discernable differences in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure20.png}
\caption{TEM comparison of substructure characteristics for (a) as-built SLM 316L and the same material annealed at (b) 800°C and (C) 900°C for 1 h. Annealing at 800°C reduces dislocation concentration without changes in cell forms and sizes, while 900°C annihilates the cells. Reprinted from Saeidi, et al.\textsuperscript{201}}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure21.png}
\caption{(a) Effect of high-temperature annealing conditions on MnS precipitate populations for SLM 316L and (b) average breakdown potentials and standard deviation for the same material along with wrought 316L (commercial) in 0.6 M NaCl at 25°C. Reprinted from Laleh, et al.\textsuperscript{146}}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure22.png}
\caption{Relationship between pitting potential of SLM 316L and annealing time in 3.5 wt% NaCl at room temperature. Reprinted from Melia, et al.\textsuperscript{147}}
\end{figure}
mass loss per the ASTM G48 FeCl₃ test. Kong, et al., reported that annealing at 650°C for 1 h resulted in severe attack of melt pool boundaries after immersion in 0.5 M sulfuric acid solutions compared to as-built and 1,050°C annealed material.¹⁴⁹ Macan-guay, et al., also reported extensive attack at SLM 316L melt pool boundaries in a persulfate sensitization test etchant after annealing at 575°C for as short as 1 h. They speculated that sigma phase precipitates at the boundaries may be responsible, but stated that detailed microstructural analysis was necessary.¹⁵⁰ Laleh, et al., found substantially lower intergranular corrosion (IGC) susceptibility of SLM 316L vs. wrought after 60 h at 700°C, attributing this to precipitation of phases in the SLM as compared to chromium carbides in the wrought material.¹⁴⁹ Further data on the effects of stress relief annealing on AM SS, including detailed microstructural information, are required for informed selection of appropriate heat treatment and welding schedules for AM components when used in corrosive service applications. Some amount of stress relief, however, appears necessary to mitigate SCC or other EAC forms in such relevant environments, see Residual Stress, section 3.7.

### 5.2 Hot Isostatic Press

Hot isostatic press (HIP) treatment at solution annealing temperatures has been used as a strategy to both homogenize microstructure and densify the material by closing pores and cracks, but with limited effectiveness regarding the latter in initial studies. Röttger, et al., subjected SLM 316L with porosity ranging from 9% to 2.5% to HIP (1,150°C for 3 h) followed by annealing and reported no reduction in porosity and partial densification of cracks.¹⁵¹ They attributed this to the pores and cracks being filled with the argon gas build atmosphere. Argon gas is negligibly soluble in steel and was postulated to be compressed in partially closed pores during HIP but can reopen pores during annealing. More recent studies, however, have shown that full densification (>99.99%) is possible using HIP for AM steel that has an initial density of >99% density.¹⁵²

The few studies to date on corrosion of HIP-treated AM SS, specifically SLM 316L, show both detrimental and beneficial effects of HIP, dependent on environment and degradation mode. Work by Geenan, et al., shows generally diminished resistance of HIP-treated SLM 316L relative to as-built in 0.5 M sulfuric acid, with activation and passive current densities 10 times higher than the as-built material.¹⁵³ The authors attributed this mainly to the effect of recrystallization and spheroidization of oxides produced by HIP, but micrometer-sized chromium carbides were also prevalent along grain boundaries. In our opinion, the chromium carbides were likely formed during the furnace cool step after HIP and could likely be avoided by quenching immediately after HIP or through an additional annealing and quench step. Concerning EAC, Lou reported comparable SCC growth behavior between solution annealed and HIP and solution annealed SLM 316L in high-temperature water.¹⁰⁹ In another study, however, the same group found that HIP reduced the irradiation assisted SCC (IASSC) susceptibility of SLM 316L by reducing irradiation damage and anisotropic behavior associated with printing texture.³⁷ The authors therefore recommended HIP for enhancing radiation tolerance and IASCC damage. Although HIP may be effective in certain situations, its expense is a limiting factor for broad application.

### 5.3 Surface Finishing

Numerous surface finishing studies using a variety of approaches have been performed attempting to alleviate AM surface roughness. Strategies include in-process approaches, laser surface modification (remelting, shock peening, etc.),¹⁵⁴-¹⁵² mechanical surface finishing (planar polishing, tumble polishing, shot peening, etc.),¹⁶³-¹⁷² and chemical and electrochemical polishing.¹⁷⁵-¹⁷⁷ Schaller, et al., showed that industrial silica grit blasting used to knock off partially fused powder caused active corrosion of SLM 304L at open circuit in quiescent 0.6 M NaCl.¹⁵⁸ They attributed this to incomplete removal of surface voids, high imparted strain, and embedded silica particles in the matrix. Chemical mechanical polishing after sand blasting has been shown to further improve surface finish and corrosion resistance of SLM SS.¹⁷⁹ A systematic study of several types of surface treatments by Melia, et al., found that a lower average surface roughness ($S_a$) imparted by a finishing technique, the higher the breakdown potential, Figure 23.¹¹⁶ Exceptions to this trend came with finishing techniques that deformed the tortuous “cling-on” features, which maintained the sharp crevice-like roughness but showed a reduction in $S_a$ value, suggesting the $S_a$ roughness metric will not capture all of the features that will be detrimental to corrosion resistance.

An overarching challenge and critical issue for any surface finishing method is the ability to effectively polish parts with complex shapes and hidden surfaces, such as lattice structures or internal channels. Urlea, et al., is one of a few groups showing the unique ability AM has at building custom cathodes for electropolishing, improving the electropolishing efficiency of these complex/hidden surfaces.¹⁷⁹ That said, the polishing of complex AM parts, such as lattices, remains in its infancy and the topic of AM part surface finishing deserves further attention.

### ADDITIVE MANUFACTURING CORROSION IN VARIED ENVIRONMENTS

Corrosion studies of AM SS to date have addressed only a limited number of environments relative to the wide range of conventional SS service conditions, from aerospace to chemical processing. Nearly all studies have been performed under short-term immersed conditions. The vast majority of these have focused on chloride media, Figure 1. Given corrosion of AM SS is an emergent topic area and aqueous chloride environments are of wide interest, this focus area could be expected.
INVITED CRITICAL REVIEW

There are several critical areas that should be addressed as research moves forward in terms of providing technical basis and assessment of corrosion performance for qualification. One of these areas is understanding the long-term performance (months, years) of AM SS in expected service environments and how it relates to the more common short-term (hours, days) laboratory studies. For example, are there preferential attack pathways that develop under natural service conditions, such as melt pool boundaries, where localized corrosion may be occurring at potentials on the edge of passivity (near \( E_{pdl} \)) rather than when it is driven at much higher breakdown potentials? How susceptible is AM SS to hydrogen embrittlement and what are long-term SCC pathways? How do these materials perform relative to their conventional counterparts under standard accelerated testing? This type of information will help to assess and develop appropriate accelerated testing and performance modeling for qualification purposes. Relatedly, information on the performance of AM SS in atmospheric environments, where its use is arguably most prevalent, is lacking.

SUMMARY AND CONCLUDING REMARKS

Understanding the corrosion performance of AM metals, particularly corrosion-resistant alloys, is an increasingly vital issue as they move from the lab to service applications. Although research on the corrosion of AM SS is in the early stages, studies to date on this topic combined with the wealth of existing SS corrosion knowledge provide substantial insight into understanding the interrelationships between AM process, structure, and environmental degradation. Still there are many open questions and critical materials issues that must be addressed for advancement and qualification of AM SS in corrosive service environments. In this review, we provide a summary of general findings synthesized from the existing knowledgebase along with critical knowledge gaps related to the process-structure-performance triad for powder-based SLM and DED stainless steels:

Material Structure

The rapid solidification rates associated with SLM and DED processing suppress growth of deleterious nonmetallic inclusions. Inclusion refinement or annihilation is responsible for the greater corrosion breakdown resistance of ground/polished SLM SS relative to similarly finished conventional SS in neutral chloride and other environments.

Additive SLM and DED alloys possess a cellular substructure with elemental microsegregation, the nature of which and its corrosion effects vary by process and alloy composition-dependent solidification behavior. The fine substructure imparted by SLM may act like that proposed for nanocrystalline metals—enhancing passivity in environments where it is operative (e.g., neutral chloride) and enhancing active dissolution in environments that promote it (e.g., oxidizing acids). The slower solidification rates of DED versus SLM can result in greater microsegregation and the associated formation of deleterious second phases, such as \( \delta \) ferrite in austenitic SS. This can negate the beneficial effects of inclusion scale-down in DED SS. Additional electrochemical data that isolate specific microstructural features via local electrochemical techniques and AM process manipulation would help to further elucidate their contributions to global corrosion behavior. Local techniques would help determine corrosion variability caused by microstructural features varying within a single build and from build-to-build. Corrosion performance variability from part to part will also be influenced by powder feedstock characteristics and powder reuse, both lacking systematic studies.

Melt pool boundaries, another AM-unique feature, can undergo severe selective attack in oxidizing, acidic environments. The reason for this remains unclear and its consequence on material structural integrity remains unexplored. The few studies on EAC of AM SS have not directly examined MPB effects, but do demonstrate that AM solidification features, including substructure and oxides, can strongly influence EAC behavior.

Defects

Pores, particularly lack of fusion pores, can control corrosion behavior to the first order by serving as a crevice-like features wherein corrosion preferentially propagates. Bulk material porosity is used ubiquitously in the AM community to optimize processing parameters. It is an unreliable indicator of corrosion resistance, as it does not capture pore morphology and distribution—two critical factors controlling corrosion susceptibility. Most studies have focused on defects in bulk AM material, however, retention of the as-printed surface may be necessary or desired for some applications. The characteristically defective as-printed surfaces can have considerably poorer corrosion resistance than finished conventionally processed SS; surface finish remains a challenge. Further understanding the causal linkage between bulk and surface defect characteristics on corrosion and EAC susceptibility will be imperative for AM process optimization, qualification, and fitness for service efforts.

Residual Stress

Laser-based fusion processes inherently introduce residual stresses into built parts that can exceed the nominal yield strength of the material. Studies to date suggest that compressive stresses in AM SS are beneficial toward pitting resistance, but near-surface tensile stresses in built components have been largely overlooked. Literature has shown that as-printed parts can be especially vulnerable to chloride-induced SCC. Future studies should address these issues. The impact of residual stress on corrosion and EAC susceptibility should be considered during part design, manufacture, and qualification.

Heat Treatment

The thermal stability and evolution of AM SS microstructures are considerably different from conventional SS. Solution annealing can eliminate many of the AM-unique microstructural features (e.g., MPBs, substructure) save for porosity and nonmetallic inclusions. Additionally, it may promote precipitation and growth of detrimental nonmetallic inclusions or other secondary phases. The effect of stress relieving on corrosion is less clear, although it appears that AM austenitic SS can have considerably different sensitization susceptibility than conventionally processed SS. Further data on how annealing AM SS affects corrosion and mechanical properties together, including detailed microstructural information, are required for informed selection of appropriate heat treatment for these materials. Some amount of stress relief, however, appears necessary to mitigate SCC or other forms of EAC.

Modes and Environments

Corrosion studies of AM SS to date have addressed only a limited number of environments and corrosion degradation modes relative to the wide range of conventional SS service conditions. EAC, particularly corrosion fatigue, has received little attention despite common issues in these areas with conventional SS. Furthermore, information on the long-term corrosion performance of AM SS along with accelerated testing...
strategies will be an integral component of AM qualification, especially for high consequence, high reliability systems.

**Material Advancement Opportunities**

An exciting and relatively open research area is utilization of additive processing to create AM metallic materials, including SS, that exceed the corrosion performance of conventional alloys. For example, how can we utilize extreme cooling rates and high-fidelity heat input control to create desirable microstructures, such as corrosion resistance enhancing textures or metallic glass surfaces? Design of new AM-tailored alloys that can mitigate defect issues and generally enhance corrosion resistance relative to conventional alloys is another open area. The parameter space afforded by SLM and DED processing could be further utilized to rapidly explore corrosion behavior across microstructure and compositional space via graded materials. Surface cladding (multimaterial approaches) and the development of metal matrix composites are additional AM design strategies that could prove fruitful for enhanced corrosion resistance.

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**DATA AVAILABILITY**

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

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