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Impact of Support Dissolution on the Corrosion Resistance of 316L Stainless Steels

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ABSTRACT

Metal additive manufacturing (AM) generally requires removal of support structures through costly post processing which may limit part design and complexity. A novel process developed at the Colorado School of Mines has dramatically simplified post processing by sensitizing and selectively corroding support material. While this process has been proven for 316L stainless steel, the corrosion response of the stainless steel after etching is unknown. To determine whether the corrosion-resistant properties of the stainless steel are maintained, this paper evaluates additively manufactured 316L stainless steel specimens after they have undergone the sensitization and etching process. The corrosion response in NaCl of 316L laser powder bed fusion (L-PBF) parts were evaluated as a function of build orientation and post-processing parameters. Electrochemical data was combined with metallographic analysis to connect corrosion mechanisms to the underlying microstructure and, ultimately, the processing conditions.

Key words: corrosion resistant materials, metals, additive manufacturing, electrochemistry

INTRODUCTION

Additive manufacturing (AM) has been identified as a potential pathway for fabricating obsolete mechanical components on the US Bureau of Reclamation's (Reclamation) aging infrastructure. Although Reclamation could develop the capability to print the needed metallic parts, post-processing of the complex geometries could be costly, time consuming, may not yield required design tolerances, and could initiate deleterious effects, such as corrosion.

The cost for post-processing of AM parts includes the labor and equipment to remove the structural supports that support a piece during the powder bed fusion process, and can account for more than 45 percent of the total cost of printing.¹ One novel solution to simplify post-processing was developed by Dr. Owen Hildreth at the Colorado School of Mines.² In this method, the chemical stability of the top 100-200 μm of the part's surface is decreased through sensitization and is carburized during thermal annealing by exposing the part to sodium hexacyanoferrate (II) decahydrate ($\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$) under certain heating conditions. The surface is made sensitive to chemical and electrochemical dissolution when the protective chromium in chromium carbide precipitates is captured during the reaction. Then, only the carburized layer of the part is selectively corroded when the entire part is submerged in a solution of nitric acid (HNO_3) and potassium chloride (KCl) and subjected to an anodic bias. On parts intended for service, support structures can be designed to be less than 200 μm in width so that they can be dissolved away by utilizing this method.

While the support dissolution process is proven to be successful at removing support material from stainless steel parts, it is unknown whether the corrosion resistance of the parts is maintained or if additional heat treatments are necessary to dilute any remnant carbon and restore corrosion performance. This paper evaluates laser powder bed fusion (L-PBF) additively manufactured 316L steel specimens after they have undergone the sensitization and dissolution (etching) process. The corrosion response of 316L powder bed fusion parts in sodium chloride (NaCl) was evaluated as a function of post-processing parameters to better understand the material-process-structure relationship. This work also evaluated the surface roughness of a part before and after support dissolution. The goal of this work was to optimize the feasibility of using AM to print metal parts while ensuring printed parts could be utilized in Reclamation's corrosive service environments.

EXPERIMENTAL PROCEDURE

316L specimens were disks approximately 15-mm in diameter and 4-mm thick. Specimens were prepared for evaluation techniques including electrochemical testing (open circuit potential, OCP), metallography to evaluate grain structure, and contact profilometry. The manufacturing technique, post-processing technique, and evaluation technique for each specimen type are given in Table 1.

Table 1
Manufacturing and post-processing techniques for tested specimens

Manufacturing Technique	Post-Processing Technique	Evaluation Technique	
		Polished	Unpolished
Cold rolled	N/A (as-received, AR)	Metallography, OCP	Profilometry, OCP
AM (PBF)	N/A (as-printed, AP)	Metallography, OCP	Profilometry, OCP
AM (PBF)	Sensitization/chemical etching (ETCH)	Metallography	Profilometry, OCP

Specimen Preparation

The cold rolled 316L stainless steel specimens were commercially obtained. Specimens were sequentially ground using 180, 320, 400, 600, and 800 grit silicon carbide paper (Leco[†]) and polished to one micron (mirror finish) using 6 μm and 1 μm diamond suspension. All grinding and polishing supplies were used as received. Additional specimens were tested in the as-received (unpolished) condition. Specimens were ultrasonically cleaned for five minutes in isopropyl alcohol and dried with gaseous nitrogen (N_2) immediately prior to any testing.

The AM 316L stainless steel specimens were manufactured with an EOS M290[†] Direct Metal Laser Sintering (DMLS) printer. The default printing parameters were as follows: 100 W laser power, 675 mm/s scan speed, and 40 μm layer thickness. Specimens were ground and polished to one micron with a diamond suspension as detailed above. Additional specimens were utilized in the as-received (as-printed) condition. Specimens were ultrasonically cleaned for five minutes in isopropyl alcohol immediately prior to any testing.

The sensitized/chemically etched specimens were prepared according to the method described in Lefky, *et al.*² To sensitize the printed 316L stainless steel specimens, a saturated solution of $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ and deionized water was prepared. In addition, a paste of 4.2 parts by mass $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ and one-part deionized water was also prepared. The specimens were submerged in the saturated solution for 20 minutes and then completely coated with the 4.2:1 paste and graphite powder. The coated specimens were wrapped tightly with a high temperature 309 stainless steel tool wrap. A small hole, approximately 0.1-mm in diameter, was punched into the corner of the tool wrap to allow for the release of cyanide and water vapor that is formed during the decomposition of the paste. The tool wrap-and-specimen package was placed in a Lindberg Model C10[†] silicon carbide box furnace at room temperature. The furnace was heated with a ramp rate of 5 $^\circ\text{C}$ per minute to 800 $^\circ\text{C}$. The package remained at that temperature for six hours; then, the furnace was turned off and allowed to cool to room temperature.

To etch the sensitized specimens, they were first removed from the tool wrap package and ultrasonicated in deionized water for five minutes. The specimens were then secured in a specially made sample holder to only etch a portion of the disk. An electrolyte solution of 0.48 molar concentration HNO_3 and 0.1 molar concentration of KCl was prepared. The electrolyte was poured into a corrosion cell and the specimen in the sample holder was placed into the cell. A silver/silver chloride (Ag/AgCl) reference electrode was ionically connected to the electrolyte through a KCl salt bridge. The counter electrode was a 6.35-mm diameter graphite rod.

A Princeton Applied Research Parstat MC[†] potentiostat was utilized to perform chronoamperometry with a potential of -0.01 Volts (V) for 60 seconds to clean the specimen's surface. The open circuit potential (OCP) was then measured for 300 seconds and cyclic voltammetry curves were generated with a scan rate of 0.01 from ± 0.1 V around the OCP. Finally, the etching process was initiated through chronoamperometry at a potential of 0.2 $\text{V}_{\text{Ag}/\text{AgCl}}$ for a duration of 50 hours.

Each PBF specimen type included specimens printed at 0, 45, 60, and 90-degrees ($^\circ$) to the build platform. The chemical compositions of the cold rolled and printed stainless steel specimens, determined via Auger Electron Spectroscopy, are in Table 2.

[†] Trade name.