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Comparison of the effects of a sulfuric acid environment on traditionally manufactured and additive manufactured stainless steel 316L alloy

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ABSTRACT

The effects on the surface and mechanical properties of stainless steel AISI316L dogbones created using either traditional manufacturing (TM) or laser powder bed fusion (LPBF) exposed to 0.75 M sulfuric acid solution over 2184 h were studied. General corrosion was not a major form of corrosion, based on surface feature changes, surface roughness, and mass loss for either method. No change to the mechanical properties occurred for the TM samples. Both tensile stress and strain decreased for the LPBF samples. The decrease was caused by hydrogen embrittlement, due to the formation of large brittle particles, as demonstrated by scanning electron microscopy.

1. Introduction

Stainless steels, which are steel alloys containing a minimum of 11% chromium by weight [1], are incredibly versatile because they have the strength of typical steel products while also remaining resistant to many corrosive environments. The chromium passivates in the presence of oxygen to form a thin layer of chromium oxide, which protects the metal underneath [2]. This film reforms even if the surface of the metal is scratched or damaged. Within the various grades of stainless steel, the 300 series contains at least 16% chromium and 6% nickel by weight [3]. The specific grade in this research, SS 316L, contains 16–18% chromium, 10–14% nickel, 10% nitrogen, 2–3% molybdenum, 2% manganese, and 0.3% carbon by weight, as compared to 0.8% by weight in 316 [4]. SS 316 is used in environments where both strength and corrosion resistance are required, such as aerospace, pharmaceuticals, cutlery, and marine applications [5], while SS 316L is used for improved performance under corrosive environments, especially where potential leaching of carbon from the steel would decrease strength [1].

Because of the mechanical properties and corrosion resistance of stainless steel, various grades are currently being investigated for use in Additive Manufacturing (AM), which can build complex parts layer-by-layer [6]. AM has experienced vast improvements in recent years, by decreasing porosity and improving mechanical properties of a variety of metals [6]. Previously, the parts produced were more porous, with altered mechanical properties, including reduce tensile stress, strain, and brittle fractures [7,8], caused by differences in laser power, laser speed, and powder production processes [9,10]. Within AM, there are multiple methods of deposition, including Laser Beam Melting (LBM), Electron Beam Melting (EBM), and Laser Metal Deposition (LMD) [6]. Within the LBM group is laser powder bed fusion (LPBF), which uses a metal powder laid out in a very thin layer, usually around 20–100 μm thick [6,11]. A laser above the stage is used to heat the powder until it nearly melts and then solidifies [6,12]. After the powder solidifies and before another layer of powder is laid down, all of the loose powder is recycled back into the printer, the stage moves down, another powder layer is applied on top of the solid layer, and the laser is activated to melt the new powder layer. This process is repeated, building the item layer by layer, with the geometries specified in the SolidWorks or Computer-Aided Design (CAD) file. As with all AM methods, LPBF gives manufacturers the ability to print out a single metal part with intricate geometries that would be impossible to produce using traditional machining techniques, as well as eliminating nearly all wasted material typically produced in traditional machining processes [13]. LPBF differs from Selective Laser Melting (SLM), which is also a type of LBM, because the parts are made in an environment of inert gas [14].

One of the major drawbacks of AM stems from the manufacturing process, since the metal powder is not melted and solidified in the same way as traditional manufacturing methods. Specifically, due to the rapid solidification and cooling, the molecules in the metal are arranged differently, in higher energy state, resulting in high residual stresses within the metal [15–17]. With LPBF and other LBM methods, the initial layer contains melt pools comprised of supersaturated metal, since the elements could not diffuse to different locations due to the rapid cooling [18,19]. However, because the laser heats up the metal powder

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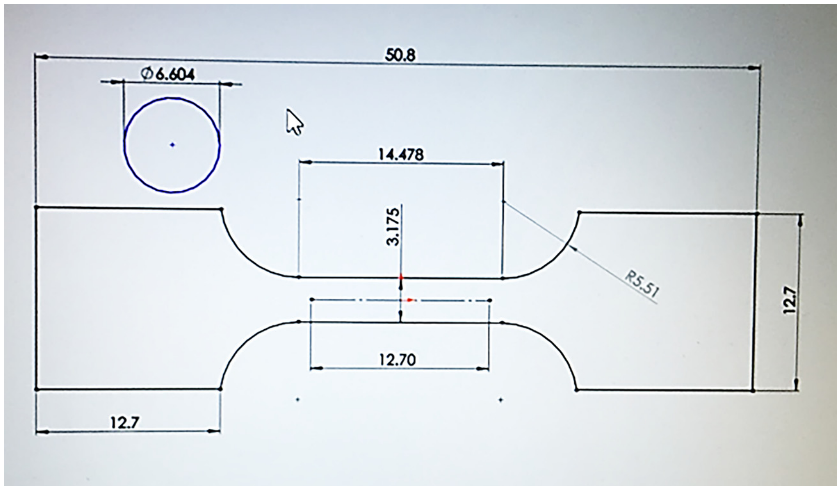

Fig. 1. Dog Bone dimensions used to produce LPBF samples and TM samples, with all dimensions in millimeters. Dimensions are scaled down from ASTM E-8 standards [34].

as it is melted, the layers underneath the laser also experience heating, allowing for diffusion of the elements to different locations, causing higher concentrations of these elements along the edges of the melt pools [18–20]. This preferential diffusion can lead to higher rates of corrosion, as the elements that are added to reduce corrosion of stainless steel, such as chromium or molybdenum, can concentrate along the edges of the melt pool [18,20].

The research on the corrosion behavior of stainless steels produced by additive manufacturing is just beginning. With respect to the corrosion behavior, samples produced by AM methods exposed to chloride containing environments have shown to be slightly more noble than traditionally manufactured samples [20], with more susceptibility to pitting [20,21], higher pitting potentials (E_{pit}), indicating less susceptibility to pitting [22], lower repassivation potentials (E_{rep}), indicating difficulty in initiating repassivation for the AM samples [20–22], and lower break-down potentials (E_b), indicating an easier break down of the oxide film [20,21]. With this combination of behavior, the breakdown of the oxide film occurring sooner and repassivation taking longer, the metastable pits that form prior to the pitting potential degrade the surface prior to true pit initiation and growth, leading to greater corrosion degradation of the AM samples [20–22].

While the study of corrosion of 316L AM parts in chloride containing environments is minimal and ongoing, the study of corrosion of 316L AM parts in sulfuric acid is non-existent. Typically, stainless steels are not considered good materials of construction to use with sulfuric acid environments, especially as temperatures increase [23,24]. However, because the stainless steel could be located in an environment where sulfur oxidizing bacteria (SOB) exist, sulfuric acid could be produced, leading to microbial influenced corrosion [25], even when the stainless steel is not being used for sulfuric acid transportation. In addition, in the case of AM samples, the rough surface [26] can provide protection for the microbes, allowing them to reproduce, metabolize more frequently, and produce larger amounts of corrosive by-products, including sulfuric acid [25]. In addition, corrosion from SOBs is typically very localized and unpredictable, with large variations in the damage caused, which is far different from an abiotic system, where no living organisms are present and the corrosive concentrations are essentially constant [27]. For traditionally manufactured steels, sulfuric acid corrosion has been investigated, which showed that different grades experienced different effects at low concentrations of 1–2 M, but were similar at high concentrations of 6 M [28], due to the inability of the stainless steel to passivate in the higher concentrations [29]. Iron oxides were the main corrosion by-product [30], with high amounts of chromium and low amounts of manganese leading to better corrosion resistance and the formation of chromium oxides in place of iron oxides [31,32]. Hydrogen embrittlement of stainless steel in sulfuric acid environments was also a problem, where larger grains and thicker grain boundaries as compared to the laser peened surface, allowed for hydrogen to diffuse into, and collect within, the grain boundaries, resulting in a more brittle surface [33,34].

The purpose of this research, then, is to determine how exposure to a sulfuric acid solution would affect samples as-produced using LPBF compared to TM samples. The weight loss, surface effects, mechanical properties of tensile stress and strain, and fracture surfaces were determined on as-printed or as-purchased 316L using an immersion environment containing 0.75 M sulfuric acid over 2184 h. The total time of exposure was chosen as 2184 h, instead of the standard 1000 h, to ensure that the effects of the corrosive environment would be realized, as stainless steel is a slow corroding metal in sulfuric acid [30]. The ultimate goal of this research, then, is to determine how the long-term exposure to sulfuric acid affected the behavior of the stainless steel, with respect to both the surface and the mechanical properties.

2. Materials and methods

2.1. Sample preparation

Twenty-seven samples of dimensions shown in Fig. 1 in the dog bone shape modified from ASTM E-8 [35] were cut from traditionally manufactured (TM) AISI316L stainless steel (OnlineMetals.com) or printed using laser powder bed fusion (LPBF). The TM metal was used as received, with no changes made to the metal besides creating the dog bone shape. The TM dogbones were cut from a 4.76 mm thick, 12.7 mm wide, and 1219.2 mm long (0.1875″ × 0.5″ × 48″) flat rectangular bar (OnlineMetals.com). For LPBF, gas atomized stainless steel 316L powder, with a mean particle size of 30 µm, supplied by the vendor Renishaw was used. The chemical analysis for both metals are shown below in Table 1, along with the ASTM standard. A Renishaw 250AM printer (Gloucestershire, United Kingdom), located at America Makes, with a continuous wave Ytterbium fiber laser running in an inert atmosphere of Argon or Nitrogen, was used [38]. The laser ran at 200 W in a modulated operation pulsed with a TTL trigger, with a beam diameter of 70 µm at the powder surface, a scanning speed of 590 mm/sec, and an exposure time of 110 µs [38]. This produced a build rate of approximately 20 cm^3/hr [38]. After printing, the excess material in the form of supports for the parts was removed with small vice grips, ensuring that the grip thickness nor grip width were compromised. The samples were then measured with calipers to ensure that the