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CORROSION BEHAVIOUR OF ADDITIVELY MANUFACTURED 316L STAINLESS STEEL

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SUMMARY: Additive manufacturing (AM) has been the focus of innovation in manufacturing industries during the last decade owing to its advantages over traditional manufacturing, particularly its capability to build complex 3D geometries in a single step that can save a lot of time and money. Selective laser melting (SLM), as a powder-bed AM technique, builds an object at rapid solidification rates in a layer-upon-layer manner using a high-energy laser beam. This process occurs under an extremely high temperature and rapid cooling conditions, leading to a microstructure that is different from that of the conventionally-produced counterpart. Although lots of research has been devoted to understanding the physical concept of SLM processing and mechanical properties, corrosion performance of parts produced by SLM has not been sufficiently explored. In this paper, an attempt was made to explain how SLM processing influences corrosion performance of type 316L stainless steel with an emphasis on localized corrosion, intergranular corrosion, and erosion-corrosion properties. It has been found that, in the case of a high-density SLM-produced specimen, the localised and intergranular corrosion resistances showed significant improvements compared to their commercial counterpart. While the SLM-produced 316L stainless steel exhibited a weaker erosion-corrosion resistance relative to the commercial one. Mechanisms behind this unique corrosion behaviour were briefly discussed based on electrochemical tests and microscopy analysis.

Keywords: Additive manufacturing; Stainless steel; Corrosion

1. INTRODUCTION

Additive manufacturing (AM) refers to a group of methods in which a part is produced in a layer-upon-layer manner [1]. AM has gained a lot of interest in both academia and industry thanks to its advantages over traditional manufacturing techniques, especially its capability in producing intricate three-dimensional parts in a single step [2]. Amongst AM techniques, selective laser melting (SLM) is a powder-bed AM process in which a high-energy laser beam is used to locally melt the powder material to form the desired shape [3]. As a result of the layer-wise concept of SLM process, the material is being produced by this method undergoes rapid melting and solidification rates, which lead to a different microstructure from that of a conventionally-produced counterpart. Since the properties of materials such as mechanical and electrochemical properties are highly dependent upon their microstructure, the properties of additively-manufactured materials are expected to show different response to those of conventionally-produced ones.

Steels, and more notably stainless steels, have been one of the most popular metals processed by AM because of their widespread usage in structural, biomedical, oil & gas industries, to list a few [4, 5]. Although the mechanical
properties of the stainless steels produced by AM have been the focus of numerous research [2], their corrosion behaviour is still nascent and needs more investigation [6]. As a part of a continuing research program, corrosion behaviour of type 316L stainless steel produced by SLM processing was investigated in this paper. For this purpose, different types of corrosion, including localised corrosion, intergranular corrosion, and erosion-corrosion resistances, were evaluated using electrochemical measurements coupled with microscopy analysis.

2. EXPERIMENTAL DETAILS

2.1. Material and processing

Commercially available gas-atomised 316L SS powder with particle size range between 5 and 40 μm was used as a starting material for SLM processing using an SLM solution 125 HL (SLM Solutions Group AG, Germany) machine equipped with a fiber laser. The building platform was pre-heated to a temperature of 200 °C before starting the SLM process. Laser power of 150 W, scanning speed of 600 mm/s, hatch spacing of 80 μm and layer thickness of 30 μm were used as the main SLM processing parameters in the present research. The powder layers were scanned using a meander scanning pattern, which was rotated 67° between successive layers. Measurements were made on quadruplicate cubic specimens with dimensions of 1.0 × 1.0 × 1.0 mm³ were produced.

2.2. Characterisation

The relative density of the SLM-produced specimen was measured according to the Archimedes technique using an Electronic Densimeter (Model SD-200L) with a resolution of 0.0001 g/cm³, and determined to be about 99.5% ± 0.1.

For microscopy analysis, the specimens were mechanically polished to a mirror finish with the last stage being a 0.3 μm oxide polishing suspension (OPS). Scanning electron microscope (SEM ZEISS SUPRA 55V FEG) equipped with energy dispersive spectroscopy (EDS) in an operating voltage of 20 kV was used to take images from intergranular precipitates and determine their chemical composition. EBSD acquisition was performed using a ZEISS LEO 1530 FEG SEM, with a scan step size of 0.3 μm at an accelerating voltage of 20 kV. Transmission electron microscope (TEM) was employed for a detailed analysis of precipitates, using a JEOL JEM 2100F microscope equipped with an EDS detector and operated at 200 kV. EDS mapping was performed in a scanning-transmission TEM (STEM) mode using a spot size of 1 nm. For TEM analysis, thin slices with a thickness of approximately 500 μm were cut from the specimens and then mechanically ground to a thickness of around 100 μm. Discs with a diameter of 3 mm were subsequently punched from the slices and further ground using 4000 abrasive paper until their thickness was reduced to 60-70 μm. Final thinning was carried out in a twin-jet electropolishing using a Struers Tenupol 5 device. A Confocal Laser Microscope (Olympus LEXT OLS4100) was used to prepare images from the specimens before localised corrosion tests. Optical microscope (Olympus GX41) was also used to examine the intergranular attack.

2.3. Electrochemical measurements

Various types of electrochemical measurements were conducted to investigate different types of corrosion. All electrochemical measurements were carried out using a conventional three-electrode configuration comprising a saturated Ag/AgCl electrode as the reference electrode, a titanium grid as the auxiliary electrode and 316L SS specimens as the working electrode. For localised corrosion experiments, potentiodynamic polarisation test was conducted by sweeping the potential from -0.2 to +1.4 V versus open circuit potential (OCP) at a scan rate of 10 mV/min in 0.6 M NaCl solution at room temperature. For investigating the intergranular corrosion (IGC) resistance, first, the specimens were heat-treated at 700 °C for 60 h followed by water quenching. The sensitized specimens were then evaluated using a double loop electrochemical potentiokinetic reactivation (DL-EPR) test in 0.5 M H₂SO₄ + 0.01 M KSCN solution at room temperature to investigate their IGC resistance by firstly scanning the potential in the anodic direction from open circuit potential (OCP) to +0.35 V vs the reference electrode at a scanning rate of 100 mV/min and then immediately reversing to the starting point at the same scanning rate, according to ASTM G108. The degree of sensitisation (DOS) was determined from the ratio of maximum current density in the reactivation loop (I_r) to current density in the activation loop (I_a). Erosion-corrosion measurements were conducted using a jet impingement system capable of providing flow speeds up to 17 m/s and various impact angles. A 0.6 M NaCl solution containing 2.5 wt% sand particles were delivered through a nozzle impinging on the specimen surface. To investigate the depassivation/repassivation behaviour, potentiostatic measurements at the constant potential of +100 mV (vs. Ag/AgCl) were carried out during the erosion-corrosion test.
3. RESULTS AND DISCUSSION

3.1. Pitting corrosion

Figure 1 shows the potentiodynamic polarisation curves for conventionally-produced and SLM-produced 316L SS. The breakdown potential, a potential in the passive region at which the current density suddenly starts to increase with further increase in potential, for the SLM-produced specimen is considerably higher than that of its conventionally-produced counterpart. This indicates a higher resistance against pitting corrosion for SLM-produced 316L SS. Pitting corrosion is a serious problem for passive metals and alloys when exposed to corrosive environments [7-9]. For type 316L SS, pitting corrosion is believed to be mainly due to the presence of MnS inclusions, where the pits tend to initiate either from the edges of the inclusions [10] or from the inclusion itself [11]. This type of inclusion with corresponding elemental maps is displayed in Fig. 2a for the conventionally-produced 316L SS. However, for the SLM-produced specimen, no trace of MnS inclusions was detected using SEM-EDS analysis. Instead, spherical inclusions enriched in Mn, Si, Al, and O were found, as shown in Fig. 2b. The main reason for the observed difference in inclusion type could be related to the rapid solidification rates associated with SLM-processing [12]. Therefore, elimination of MnS formation is the key reason for enhanced pitting corrosion resistance of the SLM-produced specimen [13, 14].

Fig. 1. Potentiodynamic polarisation curves of the conventionally-produced and SLM-produced 316L SS recorded in 0.6 M NaCl solution at room temperature, indicating a higher pitting corrosion resistance of the SLM-produced specimen.

Fig. 2. SEM-EDS analysis of the inclusions in the conventionally-produced (a) and SLM-produced (b) 316L SS.
3.2. Erosion-corrosion

Erosion-corrosion is defined as an accelerated rate of corrosion due to the relative motion of a corrosive fluid on the metal surface [15, 16]. It is generally believed that the erosion-corrosion rate cannot be acquired by simply adding the corrosion and erosion rates, and there should be interactions between erosion and corrosion, which lead to erosion-enhanced corrosion and/or corrosion-enhanced erosion [17-20]. This makes the erosion-corrosion mechanism more complex. A common method for investigating the erosion-corrosion resistance of stainless steels is to find a critical fluid velocity above which the current density increases at a faster rate. For this purpose, potentiostatic experiments were conducted while the fluid velocity increased gradually from static conditions up to 17 m/s with a step of 1.5 m/s. The results are shown in Fig. 3 for both conventionally-produced and SLM-produced specimens. The current density is almost zero at static conditions for both of the specimens, indicating that the applied potential (+100 mV) is within the passive regions of the alloys, and capable of forming a passive film on the surface, which inhibits the material from being corroded. With the pump was turned on, the fluid started to hit the surface of the specimen and current density increased suddenly. With the fluid velocity was kept constant, the current density decreased and then remained at a constant value. This indicates that depassivation/repassivation phenomenon are occurring on the surface during impingement of sand particles. This trend (sudden increase in the current density just after an increment in the fluid velocity) was repeated after each step increase in fluid velocity. Furthermore, the SLM-produced specimen showed higher values of current densities under identical conditions, suggesting the weaker erosion-corrosion resistance of the SLM-produced specimen compared to its conventionally-produced counterpart. This is unexpected considering the better localised corrosion resistance of the SLM-produced specimen (see section 3.1) and also its higher micro-hardness (~185 HV10 for SLM-produced versus ~145 HV10 for conventionally-produced specimen). Therefore, higher localised corrosion resistance and/or higher micro-hardness values don’t necessary guarantee a better erosion-corrosion resistance in stainless steels. This is because of the presence of a passive film on the surface of stainless steels, which acts as a barrier between the metal matrix and the corrosive environment. During the erosion-corrosion test, sand particles repeatedly impinge the surface, which leads to the breakdown of the passive film, however, the passive film reforms again. The repassivation ability in the passive metals and alloys is a key factor controlling the erosion-corrosion susceptibility.

![Fig. 3. Potentiostatic polarisation measurements for SLM-produced (a) and commercial (b) 316L SS specimens recorded during the erosion-corrosion test. A 0.6 M NaCl slurry solution containing 2.5 wt% sand particles was used as the test solution. The specimens were anodically polarised to +100 mV during the test to keep them in the passive state. Every five minutes, the flow speed was increased by 1.5 m/s to reach a final speed of 17 m/s.](image)

To investigate the repassivation ability, a three-stage experiment was used in this study. In the first stage, the pump was off, which allowed the formation of a passive film on the specimen’s surface. In the second stage, the pump was turned on and the fluid impinged the specimen’s surface at a velocity of 14 m/s for 20 min. The pump was then turned off at the third stage, allowing the surface to repassivate. The variation of current density during these stages are presented in Fig. 4a and b. During the first stage, the current density is almost zero for both the conventionally-produced and SLM-produced specimens, indicating the formation of a protective passive film on
their surfaces. The current density increased when the pump was turned on in the second stage, as a result of breakdown/removal of the passive film. The average current density at this stage is high (~ 4.5 A/cm² and ~ 5.5 A/cm² for commercial and SLM-produced specimens, respectively), which shows that the depassivation dominates the repassivation during the second stage. With turning the pump off in the third stage, the current density started to decrease, which is an indication of repassivation. The rate at which the repassivation occurs is different for the conventionally-produced and SLM-produced specimens based on the slope of the I-t curve in the third stage. Drawing the inverse of current (1/I) versus time reveals this difference, as displayed in Fig. 4c and d, where the repassivation rate was measured to be 0.4383 and 0.1813 for commercial and SLM-produced specimens, respectively. This indicates that when depassivation occurs on the surface, repassivation occurs much easier and faster on the commercial 316L SS compared to its SLM-produced counterpart.

Fig. 4. Three-stage potentiostatic polarisation measurement for investigating the re-passivation ability under erosion-corrosion conditions. for (a) commercial and (b) SLM-produced 316L SS. During stage 1, the pump is switched off for 20 min. At stage 2, the de-passivation process starts by switching the pump on for 20 min. During this stage the 0.6 M NaCl slurry solution containing 2.5 wt.% sand particles continually impinged the surface of the specimens at a constant flow speed of 14 m/s. At stage 3, the pump is switched off and the repassivation process occurs. The current density inverse against time for commercial (c) and SLM-produced (d) 316L SS. Dashed lines represent the linear trendlines. Corresponding linear fits to the data are also displayed.

One possible reason for the weaker repassivation ability of the SLM-produced specimen could be the presence of residual stresses. For the SLM-produced parts, large residual stresses have been reported in the literature [21]. Heat treatment was used to relief the residual stresses, and then the erosion-corrosion tests were repeated for the stress-relieved specimen and compared with its as-built conditions (not reported here but presented in [22]). The results didn’t show any obvious difference in the erosion-corrosion resistance between the as-built and stress-relieved SLM-produced specimens. So, the residual stresses might not be a major factor contributing to the weaker repassivation ability of the SLM-produced specimen. Another possible reason for weaker repassivation ability of the SLM-produced specimen could be the presence of defects/pores. Although the SLM-produced specimen used in this study was a high-density one (~ 99.5%), there will still be some small pores inside the SLM-produced specimen, which might influence the repassivation process. This needs more detailed investigation in future work.

3.3. Intergranular corrosion
Intergranular corrosion is a serious issue for high-temperature (500-850 °C) applications of 316L SS, where the formation of secondary precipitates in the grain boundaries concurrent with the generation of adjacent chromium-depleted regions (a phenomenon known as sensitisation) which leads to intergranular corrosion when exposed to corrosive environments [23-25]. For conventionally-produced 316L SS, the chromium carbide precipitates were detected after heat treatment at 700 °C for 60 h, as shown in SEM-EDS analysis in Fig. 5a. However, interestingly, no chromium carbides were detected for SLM-produced specimens. Instead, many fine white precipitates were observed for SLM-produced specimens (Fig. 5b and c). These white precipitates were determined to be Mo-rich Laves phases using STEM-EDS analysis (Fig. 5d), which have rarely been reported for austenitic stainless steel. Therefore, SLM-produced specimens showed a different precipitation behaviour upon exposure to long-term heat treatment at high temperature (60 h at 700 °C). This precipitation behaviour will influence the subsequent IGC resistance when subjected to corrosive environments.

![Image](image.png)

Fig. 5. SEM micrographs showing the precipitation along grain boundaries for commercial (a) and SLM-produced 316L SS at the transverse plane (b) and build plane (c). The EDS analysis map of the commercial 316L is also presented. The black spherical spots in (b,c) are the inclusions, which are inherent in stainless steels produced by SLM, and are not due to the sensitisation heat-treatment. (d) A high-magnification STEM image of the precipitates for the SLM-produced specimen with its EDS elemental map analysis.

DL-EPR is a common method to quantitatively determine the IGC resistance of stainless steels [26], according to ASTM G108. It is an electrochemical test based on cyclic polarisation; a passive film forms on the surface at the forward scan by anodically increasing the potential from the open circuit potential (OCP) to the passive region, and then the dissolution of the passive film during the reverse scan from the passive region to the starting point gives rise to the reactivation peak. The SLM-produced 316L SS showed a substantially higher IGC resistance at both build and transverse planes compared to their conventionally-produced counterpart, as shown in DL-EPR curves in Fig. 6. The DOS value was measured to be about 25.70, 0.08, and 0.06 for commercial, SLM-transverse, and SLM-build 316L SS specimens, respectively, indicating that the SLM-produced specimens can be considered as non-sensitised material because of their very low DOS values. Optical micrographs of the specimens after DL-EPR measurements showed a severe attack along grain boundaries of the conventionally-produced specimen, while a slighter attack was detected for SLM-produced specimens. Therefore, a high DOS value corresponds to a deeper attack along grain boundaries and vice versa.

Grain boundary character of a metallic material plays the most prominent role in its IGC resistance [27-29]. Figure 7 shows the EBSD band contrast maps of the conventionally-produced and SLM-produced 316L SS, where black applied to the high angle grain boundaries (θ>15°), purple applied to low angle grain boundaries (2°<θ<15°), and blue and red applied to Σ3 and Σ9 CSL boundaries, respectively. Detailed analysis of the EBSD data revealed obvious differences in both grain size and grain boundary character between conventionally-produced and SLM-produced specimens, as summarised in Table 1. The average grain size based on line intersection method, was measured to be 19.2±0.7, 10.4±0.9, and 8.4±0.8 for commercial, SLM-build and SLM-transverse specimens, respectively, indicating a smaller average grain size for SLM-produced specimens compared to their conventionally-produced counterpart. It is generally believed that the DOS has an inverse relationship with the...
grain size; i.e. the smaller the grain size, the larger the total grain boundary surface area, which provides a larger number of nucleation sites for precipitates [30, 31]. However, the precipitates need to attain a critical size to cause sensitisation. In the case of fine-grained materials, e.g. the SLM-produced 316L SS in the present study, the carbon availability for every single nucleus is restricted because of the higher number of nuclei and therefore chromium carbides can’t precipitate, which is consistent with SEM and TEM analysis in Fig. 3, where no trace of chromium carbides was detected for SLM-produced specimens.

![Fig. 6](image)

**Fig. 6.** (a) DL-EPR curves for the commercial and SLM-produced 316L SS specimens recorded in 0.5 M H₂SO₄ + 0.01 M KSCN solution at room temperature. Optical images after DL-EPR tests for (b) commercial 316L SS showing that all grain boundaries got severely attacked, and SLM-produced 316L SS at transverse (c) and build (d) surfaces, respectively, indicating a negligible attack along grain boundaries.

![Fig. 7](image)

**Fig. 7.** EBSD band contrast maps of the conventionally-produced (a), and SLM-produced specimens in the transverse plane (b) and in the build plane (c). Black high angle grain boundaries (θ>15°), purple low angle grain boundaries (2°<θ<15°), and blue and red ∑3 and ∑9 CSL boundaries, respectively.

Type and length of grain boundaries also play important roles in IGC resistance. It is generally accepted that only low-angle grain boundaries and are immune from being sensitised [27, 32, 33]. The length of low angle grain boundaries and twin boundaries were measured to be larger for the SLM-produced specimens relative to commercial specimen, as depicted in Table 1, which could be considered as another reason for better IGC resistance of the SLM-produced specimens compared to their conventionally-produced counterpart.
Table 1. Grain size and grain boundary characteristics for conventionally-produced and SLM-produced specimens measured from the EBSD maps in Fig. 7

<table>
<thead>
<tr>
<th></th>
<th>Grain size</th>
<th>Grain boundary</th>
<th>0.7°&lt;θ&lt;2°</th>
<th>2°&lt;θ&lt;15°</th>
<th>15°&lt;θ</th>
<th>Σ3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventionally-produced</td>
<td>19.2±0.7</td>
<td>Fraction</td>
<td>1.0%</td>
<td>6.0%</td>
<td>92.5%</td>
<td>35.1%</td>
</tr>
<tr>
<td>SLM-produced (transverse plane)</td>
<td>8.4±0.8</td>
<td>Fraction</td>
<td>9.4%</td>
<td>4.7%</td>
<td>85.0%</td>
<td>24.8%</td>
</tr>
<tr>
<td>SLM-produced (build plane)</td>
<td>10.4±0.9</td>
<td>Fraction</td>
<td>10.7%</td>
<td>4.0%</td>
<td>84.6%</td>
<td>31.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Length</td>
<td>394.8 µm</td>
<td>2.34 mm</td>
<td>3.58 cm</td>
<td>1.33 cm</td>
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<tr>
<td></td>
<td></td>
<td>Length</td>
<td>8.23 mm</td>
<td>4.14 mm</td>
<td>7.45 cm</td>
<td>2.09 cm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Length</td>
<td>8.39 mm</td>
<td>3.14 mm</td>
<td>6.63 cm</td>
<td>2.37 cm</td>
</tr>
</tbody>
</table>

The most interesting finding in IGC resistance results presented here is the different mode of precipitation in conventionally-produced and SLM-produced 316L SS, where no trace of chromium carbides was detected for SLM-produced specimens after long-term sensitisation heat treatment at 700 °C. A possible reason for this unexpected behaviour could be the unique microstructure of the as-built SLM-produced 316L SS, which consisted of cells inside the grains. The separation of elements like Cr and Mo in the cell boundaries has been reported in the literature [5]. This unique microstructure might influence the diffusion of elements when subjected to high-temperature heat treatments. This needs more clarification in future work.

4. CONCLUSION

The corrosion behaviour of SLM-produced 316L SS was studied in terms of localised corrosion, intergranular corrosion, and erosion-corrosion resistances using various types of electrochemical measurements coupled with microscopy analysis. The unique microstructure of the SLM-produced specimen resulted in different corrosion performance compared to that of its conventionally-produced counterpart. The elimination of formation of MnS inclusions, which are nucleation site for pit initiation in commercial 316L SS, was found to be the main reason for the enhanced pitting corrosion resistance of the SLM-produced 316L SS. Erosion-corrosion tests, unexpectedly, revealed a weaker erosion-corrosion resistance for the SLM-produced 316L SS relative to the commercial specimen during the jet impingement testing, which was attributed to the weaker repassivation ability of the SLM-produced 316L SS. When subjected to high-temperature sensitisation heat treatment, Mo-rich Laves phase was formed in the SLM-produced specimens, while chromium carbides were detected for the commercial 316L SS. SLM-produced specimens were subsequently shown to have substantially higher IGC resistances compared to their commercial counterpart. The unusual precipitation behaviour and IGC resistance in the SLM-produced 316L SS were discussed based on the smaller average grain size, and high-frequency of low-angle grain boundaries and CSL boundaries in the SLM-produced 316L SS.

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6. REFERENCES