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## Original Article

# Microstructure-electrochemical behavior relationship in post processed AISI316L stainless steel parts fabricated by laser powder bed fusion



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## ABSTRACT

AISI316L stainless steel components produced via additive manufacturing techniques have quickly found new applications across several industrial sectors. However, parts manufactured through this method generally exhibit poor surface quality and performance in the as-built state. This work addresses the influence of laser polishing and water jet assisted recirculating shot peening on the surface quality, microstructure and electrochemical properties of AISI316L samples produced by the laser powder bed fusion method. To do so, surface roughness analysis, residual stress measurement, scanning electron microscope and electron backscatter diffraction analysis were employed along with electrochemical tests, including cyclic potentiodynamic polarization, electrochemical impedance spectroscopy and Mott-Schottky analysis. Laser polished samples exhibited a smooth surface with high tensile residual stress on the surface, which led to the reduction of pitting potential and formation of passive layers, including more crystal defects. Microscopical analysis evidenced that the higher density of lattice defects and local microstrain on the surface of the shot peened samples promoted surface hardness and induced compressive residual stress. Therefore, the shot peened samples exhibited a wider passive range in cyclic potentiodynamic polarization measurements, higher polarization resistance in electrochemical impedance spectroscopy measurements, and less defective passive film in Mott-Schottky analysis. Moreover, it was calculated that the passive film thickness of the shot peened sample was slightly larger than the other samples. Low surface roughness, high crystal defect density, and compressive residual stresses

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enhanced the passive layer's resistance to defect transport, lowered the point defect concentration in the passive film, and improved the pitting resistance of the samples.

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## 1. Introduction

Additive Manufacturing (AM) technique has grown exponentially in development and application thanks to its capability to build complex design objects [1,2]. Recently, AM has emerged as a mainstream means of producing near-net-shaped metallic components from a variety of metallic alloys with minimal waste and post-machining requirements [3,4]. Metal AM processes are primarily divided into two categories: powder bed fusion (PBF) processes, where a spread powder bed is fused via applying predefined laser or electron beam patterns. This includes laser powder bed fusion (L-PBF) and electron beam powder bed fusion (EB-PBF) [5,6]. The second category is directed energy deposition (DED), in which both the material and energy are supplied simultaneously to fabricate a vast range of metallic alloys [7–9]. It is worth mentioning that the final properties of metal AM are a function of the processing parameters. In General, the AM process variables govern the nature of the microstructure and defects formed in the as-built metallic parts [10–12]. Moreover, in some cases, a post-fabrication heat treatment may be requested to eliminate the defects and improve the service performance of the AM parts [13,14].

Due to their outstanding corrosion resistance and desirable mechanical performance, stainless steels are among the most widely researched alloys in the metal AM research field [15,16]. Austenitic grades of stainless steel have been the subject of many research and publications, with AISI316L being one of the most commonly utilized engineering alloys in industrial applications [11,17–20].

Research on the corrosion characteristics of AM stainless steels under various service conditions has increased over the last few years. As reported by several researchers, the pitting

corrosion resistance of high-density AM austenitic stainless steel is substantially higher than conventionally produced counterparts [21–23]. Nevertheless, AM components generally exhibit inadequate surface quality in the as-built state [24]. In addition, significant temperature gradients during rapid solidification of the layers may lead to undesired residual stresses [25,26]. Furthermore, different metallurgical, physical and mechanical factors such as microstructure [27,28], distribution of constituent phases and solute segregation [14,17,22], porosity [17], inclusions [29–31], residual stress [32–34] and surface roughness [21,35,36] can significantly affect the corrosion and mechanical behavior of metal AM parts.

In general, a number of solutions including parameter optimization [11,37,38], preheating the feedstock and substrate material [23], post annealing and applying severe plastic deformation (SPD) [23,39–42] were implemented to mitigate the issues caused by microstructural characteristics in AM stainless steels regarding their electrochemical performance.

In recent years, much attention has been devoted to surface modification of AM products via post-treatment [43–47]. Understanding and controlling the surface features using post-treatments is a nascent field with little progress to date for metal AM parts in a wide range of applications. However, up to date, far too little attention has been paid on the quantitative relationship between post-processing surface treatment features and corrosion properties of L-PBF AISI316L.

Hence, in this work, the aim is to quantitatively investigate, for the first time, the relationship between surface integrities and electrochemical behavior of AM AISI316L parts treated by laser polishing as a thermal surface treatment and shot peening as a mechanical surface treatment. The treated and untreated AM samples will be analyzed and compared through different characterization methods, such as 3-D

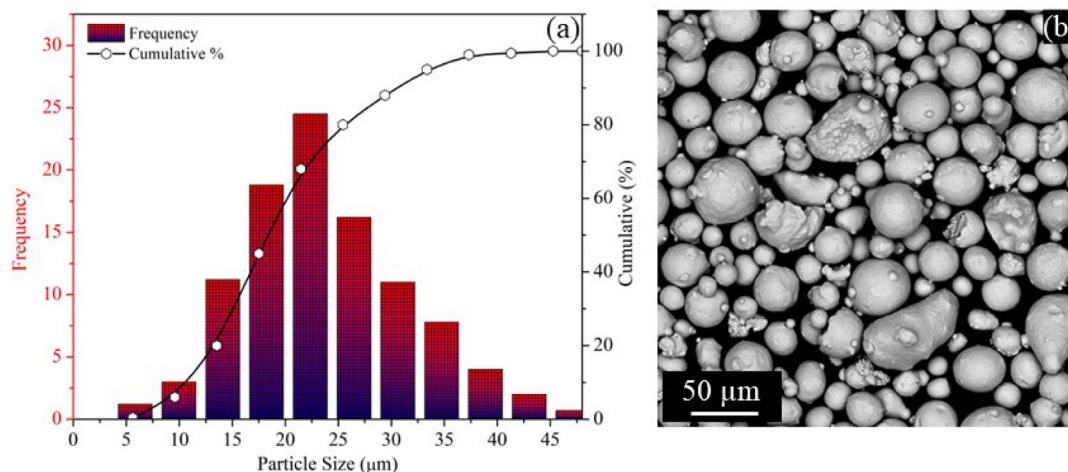


Fig. 1 – (a) Particle size distribution histograms, (b) SEM micrograph of the initial AISI316L powder.

**Table 1 – Nominal chemical composition of both the AISI316L wrought sample and the powder feedstock utilized in this study.**

Elements	Cr	Ni	Mo	C	Mn	Si	P	S	Fe
Wrought (wt.%)	16–18	10–14	2.0–3.0	0.03	2.0	0.5	0.025	0.01	Bal.
Powder (wt.%)	17.72	13.50	2.04	0.02	2.21	0.48	0.022	0.01	Bal.

profilometry, residual stress measurements, scanning electron microscopy, and corrosion tests.

## 2. Materials and methods

### 2.1. Sample preparation

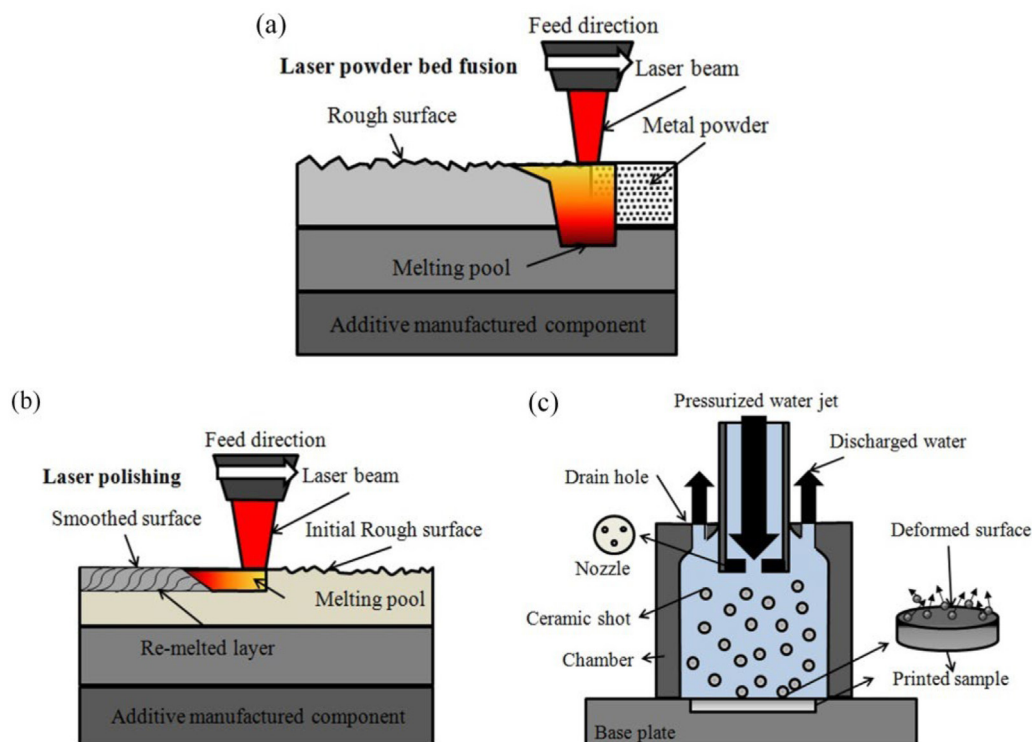
Gas-atomized AISI316L spherical powder (ECKART TLS GmbH, Germany) with an average size of 27  $\mu\text{m}$  and size distribution of 15–50  $\mu\text{m}$  was used as the feedstock material. Fig. 1 shows the morphology and particle size distribution ( $d_{10} = 12.5 \mu\text{m}$ ,  $d_{50} = 20 \mu\text{m}$ ,  $d_{90} = 32.5 \mu\text{m}$ ) of the initial powder. Wrought material were used as reference samples for comparative study. The chemical compositions of both wrought and powder AISI316L are presented in Table 1.

Cylindrical samples with a diameter of 12 mm and height of 4 mm were built using a Concept-Laser Mlab-cusing-R system equipped with a 100 W fiber laser having a beam spot size of 50  $\mu\text{m}$ . A laser power of 95 W, a laser scan speed of 500 mm/s, and hatching distance of 100  $\mu\text{m}$  were used as the standard parameters to produce the L-PBF samples. Before the L-PBF process, the building chamber was purged with argon gas to maintain the oxygen content of the chamber lower than

0.2% throughout the building operation. The schematic of the manufacturing process is shown in Fig. 2(a). The parts were then cut off from the building platform using a wire electric discharge machine (WEDM). The density evaluation of the samples following the Archimedes method verified that all the samples in the as-built state had a relative density of more than 99.5%.

### 2.2. Post-processing treatments

Laser polishing and recirculating shot peening accelerated by a water jet were used to improve the surface quality of the L-PBF samples. Upon completion of the AM process, the top surface of the as-built AISI316L samples were processed by laser polishing using a laser power of 70 W and a scan speed of 400 mm/s. For shot peening, the surface of the sample was shot peened for 20 min using a set-up similar to the one proposed by Naito et al. [48]. In summary, the surface mechanical treatment was a recirculating shot peening (hereafter called as shot peening) process utilizing balls (typically 1–6 mm diameter) made of stainless steel or ceramic. During the process, the surface of the samples is repeatedly impacted in random directions, and the shots are accelerated by a water jet with an injection pressure of 10 MPa. In this study, the



**Fig. 2 – The schematic of (a) laser powder bed fusion process, (b) laser polishing, and (c) shot peening.**

peening set-up was a home made system and 250 Zirconia ceramic shots with a smooth surface finish of  $0.04 \mu\text{m}$  ( $R_a$ ), 5 mm diameter, and hardness of  $1100 \text{HV}_{0.1}$  were used for the surface treatment. The schematic of laser polishing and shot peening are shown in Fig. 2(b) and (c), respectively.

### 2.3. Material characterization

Non-contact 3D optical surface profiler (Zygo NewView 9000, United States) was used to investigate the effect of post-treatment on surface morphologies. Measurements were performed on a single field of view, with a Mirau  $20\times$  objective (field of view of  $2 \text{ mm} \times 2 \text{ mm}$ ). The surface properties were analyzed according to the ISO25718 standard.

For microstructural examinations, the samples were first cross-sectioned, mounted in epoxy, ground down to 4000# grade SiC paper, and then polished with  $1 \mu\text{m}$  diamond paste and  $0.3 \mu\text{m}$   $\text{Al}_2\text{O}_3$  suspension. Finally, the samples were electropolished in ethanol and perchloric acid (8:2 vol/vol) solution at a direct current voltage of 20 V for 20 s. The microstructure of as-polished samples was studied in terms of the grain size evolution, grain boundary, and kernel average misorientation (KAM) using electron backscatter diffraction (EBSD) analysis and field-emission scanning electron microscopy (FE-SEM, Zeiss Sigma 500 VP). All the EBSD analyses were performed with an accelerating voltage of 25 kV and 100 nm scanning step size. EDAX OIM Analysis™ software was used to analyze the raw data obtained from the EBSD analysis.

Surface residual stresses (RS) were estimated by the X-Ray Diffraction (XRD) technique and the standardized  $\sin^2\psi$

method in the top surface of each sample, perpendicular to the build direction (BD), based on the relative position of the diffraction peak for  $hkl=(042)$  in the austenite lattice plane, which nominally appears at  $2\theta = 144.62^\circ$  for AISI 316 L. The used X-ray elastic constants are  $S_1 = -1.39 \times 10^{-6} \text{ 1/MPa}$  and  $\frac{1}{2}S_2 = 6.27 \times 10^{-6} \text{ 1/MPa}$  with the assumed material constants  $E = 190 \text{ GPa}$  and  $\nu = 0.3$  [25,49].

Vickers microhardness measurements were performed on the top side of the samples using a diamond Vickers indenter under a load of 25 g that was applied for 15 s. A total of five measurements were carried out at different treated zones, and the average values were reported together with their standard deviations.

### 2.4. Electrochemical testing

The electrochemical experiments were performed on the as-printed, post-processed (laser polished or shot peened), and wrought AISI316L samples in a 0.9% NaCl solution at room temperature. Electrochemical measurements were controlled by a PARSTAT 2273 advanced electrochemical system with a conventional three-electrode cell system in which Ag/AgCl (Sat. KCl) acted as the reference electrode (RE) with the platinum foil and the metal surface acted as the counter electrode (CE) and the working electrode (WE), respectively. As-printed samples were used to examine the corrosion resistance affected by the original residual stress state and surface roughness. In addition, an as-printed sample's surface was ground to a 2000# grit finish before electrochemical tests to separate the effect of the surface roughness from that of residual stresses. Two series of laser polished and shot peened

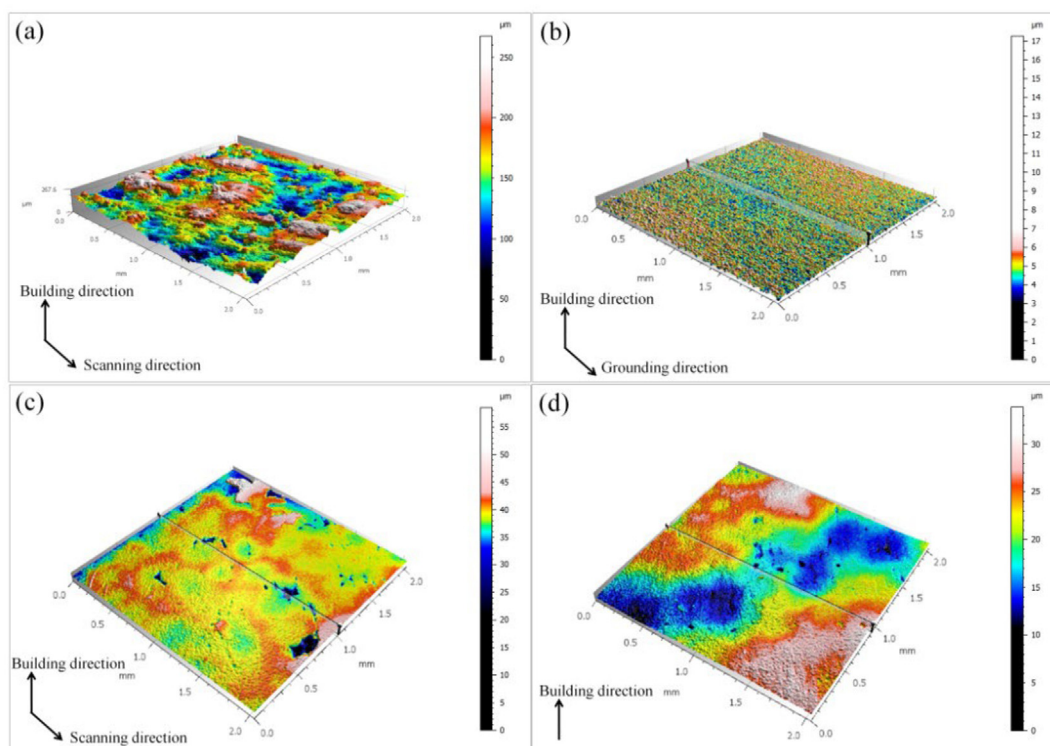


Fig. 3 – 3D surface topographies of the (a) as-printed, (b) ground, (c) laser polished and (d) shot peened samples.



samples were also analyzed with no grinding. Before the electrochemical tests, all the samples were thoroughly cleaned with ethanol and deionized water in an ultrasonic bath. The samples were then immersed for 45 min in the electrolyte prior to the electrochemical tests for stabilization, during which the open circuit potential (OCP) was measured. Cyclic potentiodynamic polarization scans were carried out from a  $-0.25$  VAg/AgCl below the OCP to  $+1.1$  VAg/AgCl at a scan rate of  $1$  mV/s. The scan direction reversed when current density values reached  $100$   $\mu\text{A}/\text{cm}^2$  thresholds, and the reversed scan continued until the samples were polarised down to  $-0.25$  V below their respective OCP. Electrochemical impedance spectroscopy (EIS) was performed at open-circuit potential conditions and AC potential with an amplitude of  $10$  mV and  $100$  kHz to  $10$  mHz frequency range, with  $15$  points per decade. The equivalent circuits were generated using the electrochemical analyzer Z-View software. Mott-Schottky (MS) measurements were conducted to study the semi-conducting type of the passive film. These measurements were carried out on the passive films at a frequency of  $1$  kHz using a  $10$  mV AC signal and a step potential of  $10$  mV by decreasing the applied potential in the cathodic direction from an initial potential  $0.6$  VAg/AgCl to a final potential of  $-1.0$  VAg/AgCl. It should be noted that before the MS measurements, the samples were allowed to reach a stable corrosion potential. All the measurements have been repeated at least three times to ensure the reproducibility and consistency of the collected data.

### 3. Results and discussions

#### 3.1. Surface roughness

3D topographies and various surface roughness parameters of as-printed and post-treated samples were obtained by 3D optical profilometry.

Based on the results reported in Fig. 3, the surface roughness of the as-printed sample was significantly higher than the rest of the samples. This discrepancy can be due to the unmelted or partially melted particles on the surfaces, along with the balling phenomenon, which could be optimized by

adjusting the processing parameters. Compared to the as-printed sample, the top surfaces of the ground, laser polished, and shot peened samples were significantly smoother. The measured roughness of the post-treated samples exhibited a decreasing trend. The lowest surface roughness belonged to the ground sample with slight grinding marks, which was approximately twenty times lower than the as-printed one. After laser polishing, most surface defects, particularly partially melted powders, were remelted, creating a smoother surface than the as-printed one. In the case of shot peened sample, most of the surface peaks were removed or flattened by the impact of ceramic shots applied in various directions. Consequently, the surface became much smoother, with some residual valleys that are typical dimples induced by multiple impacts. Indeed, shot peening not only reduces the height of the peaks on the surface but also fills valleys producing a smoother surface eventually [50,51]. However, These features, along with collision effect of ceramic shots on the surface led to the formation of a slightly rougher surface in the shot peened sample compared to the laser polished one. The surface roughness values including average mean roughness ( $S_a$ ) and maximum height of the roughness ( $S_z$ ) of corresponding samples are compared in Fig. 4.

The average surface roughness parameter,  $S_a$ , for the as-printed sample was  $14.11 \pm 1.65$   $\mu\text{m}$ , which was reduced for the ground sample to  $0.51 \pm 0.25$   $\mu\text{m}$ , and for the laser polished and shot peened samples to  $1.09 \pm 0.46$   $\mu\text{m}$  and  $1.66 \pm 0.34$   $\mu\text{m}$ , respectively. The difference between the maximum peak and valley ( $S_z$ ) was  $240.19 \pm 9.67$   $\mu\text{m}$  for the as-printed sample. This feature was measured to be  $17.44 \pm 3.31$   $\mu\text{m}$ ,  $22.25 \pm 4.25$   $\mu\text{m}$ , and  $58.52 \pm 8.46$   $\mu\text{m}$  for the ground, laser polished, and shot peened samples, respectively. Therefore, it could be concluded from these results that post-processing is a very effective way to reduce the surface roughness of the AM parts. Among the two proposed methods in this study, laser polishing would be a better candidate to achieve lower surface roughness by choosing optimal parameters. However, shot peening-based methods, in addition to the surface smoothing, can also improve mechanical and corrosion properties, which is an important advantage over the laser polishing process [23,50–52].

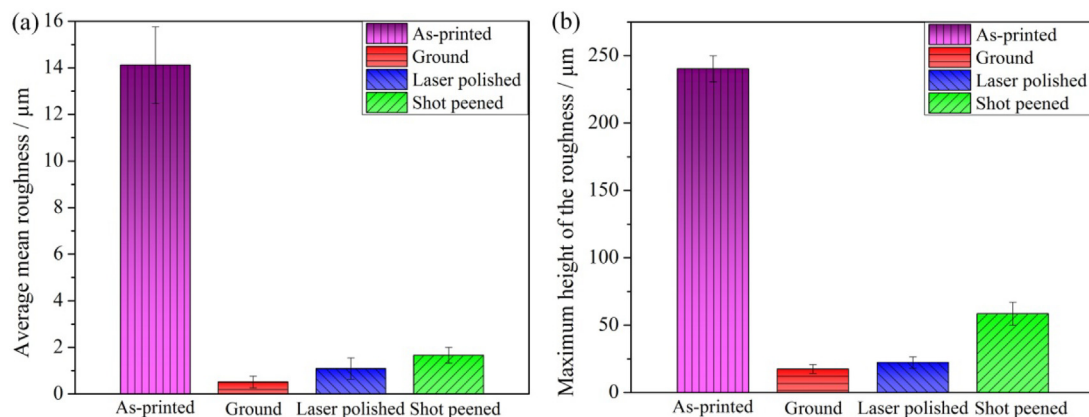


Fig. 4 – Surface roughness values of samples (a) average mean roughness ( $S_a$ ) (b) maximum height of the roughness ( $S_z$ ).

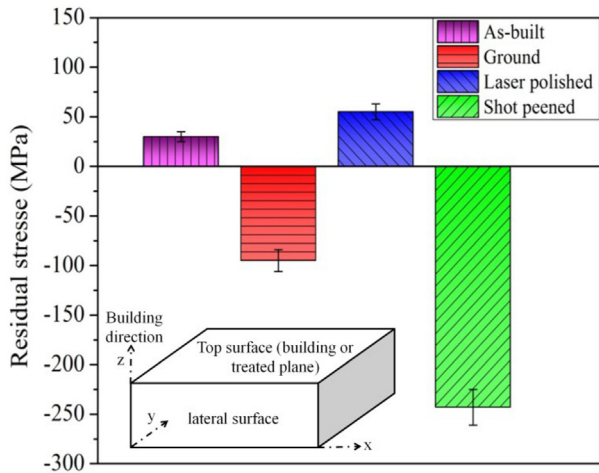


Fig. 5 – Average top surface residual stress for the samples.

3.2. Residual stress

The results of the surface residual stress measurements in the XY plane transverse to the BD by XRD analysis, are shown in Fig. 5. Tensile stresses were measured for the as-printed (30.6 ± 5.8 MPa) and laser polished (55.4 ± 8.1 MPa) samples. Simson et al. [25] reported that residual stresses on the top surface of L-PBF AISI316L samples were approximately 200 MPa. The authors reported that the magnitude of the surface residual stress highly depended on the L-PBF parameters. Tensile stress may have been generated during the heating and cooling cycles, and thermal stresses resulting from temperature gradients or solidification-induced shrinkage during fabrication for the as-printed and laser polished samples [25]. In contrast to the as-printed and laser polished samples, the residual stress on the top surfaces of the ground and shot peened samples was compressive, with the stress values being -95.7 ± 11.1 MPa and -243.7 ± 18.4 MPa, respectively. This finding is consistent with a previous work [50] emphasizing the effect of shot peening on the stress mode alteration of the AM sample's surface.

3.3. Microstructural characterization

EBSD analysis revealed the grain features and distribution of crystal defects for the as-printed sample and the post-processed ones. Fig. 6(a) shows the inverse pole figures (IPF) of the as-printed sample with columnar grains parallel to the BD on the XZ plane as a result of the high thermal gradient in the building direction. This high thermal gradient is usually linked to the high conductivity of the previously deposited layer, the small size of the melt pool created by the laser, and the high temperature at the melt pool hot spot [21]. Fig. 6(b) demonstrates that grains remained parallel to the BD when the remelting process was applied despite their enlarged size and altered crystallographic orientation. However, for the shot peened sample (Fig. 6(c)), it can be seen that the as-printed sample deformed severely due to the cold work induced by the multiple impacts while the grains were rotated and refined. Hence, it can be concluded that the grain morphology is strongly affected by the post-treatments. Fig. 6(d–f) displays the grain boundary distribution of different samples. As shown in Fig. 6(e) and (f), the microstructure of the shot peened sample contained more high angle grain boundaries (HAGBs: >15) than the as-printed sample. Indeed, a cellular sub-structure with low angle grain boundaries (LAGBs: 2–15) has been commonly observed in AISI316L samples produced via AM method. The formation of cellular substructure mainly originates from rapid solidification induced material deformation [23]. Upon laser polishing, the density of low angle grain boundaries was markedly reduced, a behavior which can be attributed to the annihilation of dislocations during the laser polishing process. It can be seen in Fig. 6(f) that LAGBs tend to form in the surface and subsurface of the shot peened sample. The grain boundaries observed inside large grains are mainly LAGBs, which tend to form near the surface. Hence the grains in the subsurface region are divided into small grains and more cellular sub-structure formed by LAGBs.

The fraction of LAGBs and HAGBs and grain boundary lengths (GBL) of the samples were statistically calculated

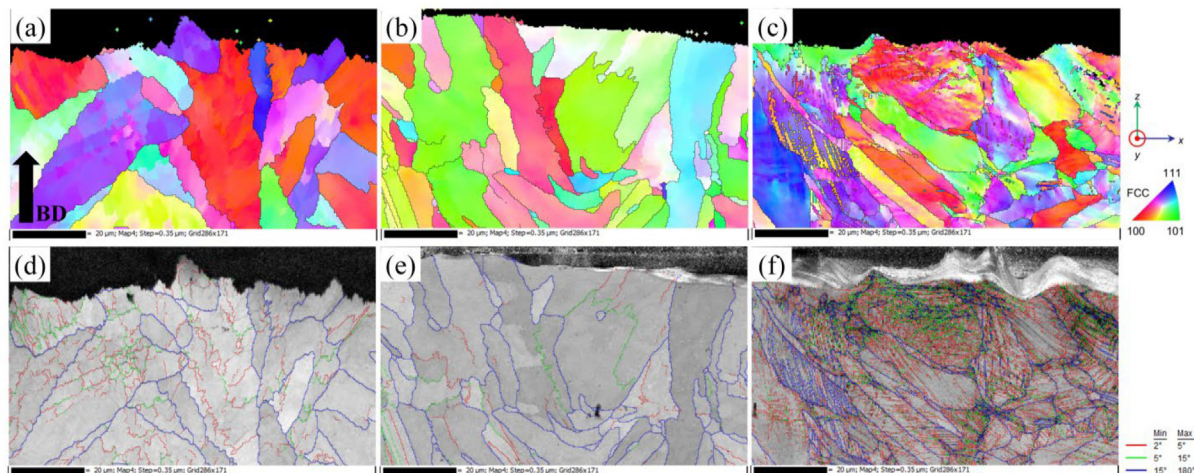
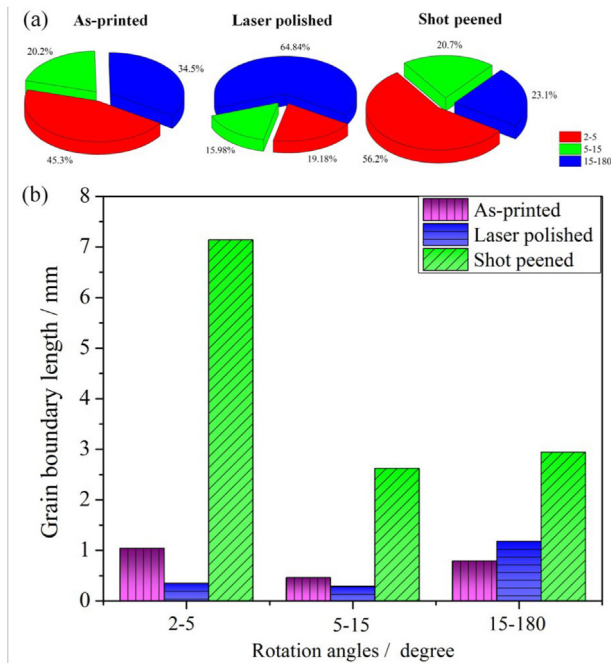


Fig. 6 – IPF images with grain boundaries: (a) as-printed, (b) laser polished, (c) shot peened, and Image quality with grain boundaries (d) as-printed, (e) laser polished, (f) shot peened.



**Fig. 7 – (a) Fraction of LAGBs and HAGBs and (b) the distribution of grain boundary length with rotation angle in the studied samples.**

based on the EBSD results approximately 50  $\mu\text{m}$  depth from the surface and reported in Fig. 7.

As shown in Fig. 7, it can be seen that the fraction of LAGBs and HAGBs on the cross-section of the shot peened sample, especially near the surface, is higher than the other two samples. Indeed, it should be noted that the HAGB fraction is greater than the LAGB fraction for the laser polished sample (as shown in Fig. 6), mainly due to the induced thermal effect and re-solidification of molten metal liquid during the remelting process. Fig. 7(a) and (b) show the length of different grain boundaries for the as-printed, laser polished and shot peened samples. As shown in Fig. 7(b), the total grain boundary length of the as-printed sample (2.29 mm) was roughly 1.2 times more than that of the laser polished one (1.82 mm). In comparison, the average length of low and high angle grain boundaries in the shot peened sample (12.70 mm) was about 7 times that of the laser polished sample.

Fig. 8 shows the KAM results of the as-printed AISI316L samples before and after post-treatment, which also depicts the dislocation distribution in the samples. According to the

KAM maps, the shot peened sample (Fig. 8(c)) exhibited higher local KAM values, normally corresponding to a lattice strain or residual stress, compared to the as-printed one (Fig. 8(a)). This results would be attributed to the high density of dislocations generated during severe surface plastic deformation by the random impact of several shots repeatedly and concurrently applied on the surface, as reported for conventional shot peening applied to standard AISI316L [53].

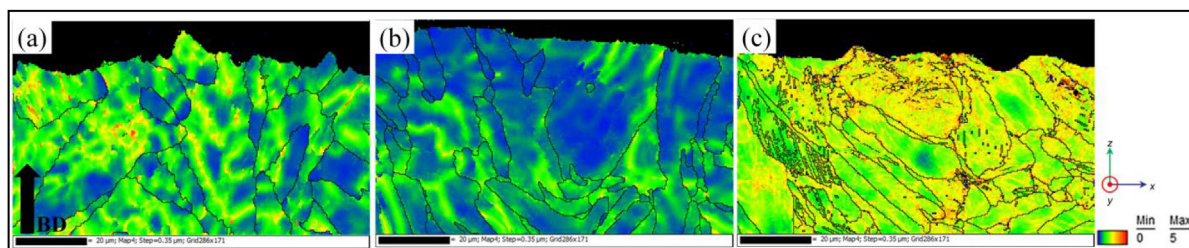
This relatively higher KAM value near the surface and subsurface of the shot peened sample corresponds also to a greater level of lattice strain or residual stress. This finding is completely in line with the outcomes of the surface residual stress analysis, which are presented in Fig. 5. However, it can be noticed that the surface strain level of the as-printed sample decreased slightly after laser polishing (Fig. 8(b)) due to the thermal input during laser polishing, which led to stress relaxation and annihilation of dislocations.

According to the microhardness results shown in Fig. 9, the surface hardness of the as-printed, ground, laser polished and shot peened samples were  $218 \pm 21$ ,  $225 \pm 19$ ,  $208 \pm 11$ , and  $284 \pm 12$  HV, respectively. After shot peening, the hardness of the sample was much higher than the as-printed and other post-processed samples. The grain boundaries and dislocation cells (Fig. 6(f)) can retard or block the migration of newly formed dislocations under external force, increasing the hardness and tensile strength [23,50].

Table 2 summarizes the investigated surface features, including roughness parameters, surface residual stress, microhardness, the fraction of LAGBs and HAGBs, and grain boundary lengths for the studied samples. The following section is dedicated to describe how these surface properties and microstructural changes influence the electrochemical behavior of the samples.

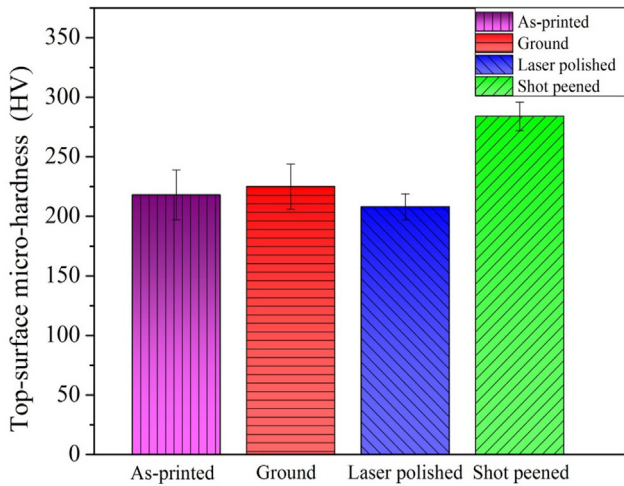
### 3.4. Open circuit potentials and cyclic potentiodynamic polarization tests

Representative open circuit potentials versus time for the as-printed sample and post-processed counterparts immersed in 0.9 wt% NaCl solution are plotted in Fig. 10(a). All the samples except for the as-printed one display similar electrochemical potential evolution tendency during immersion. In fact, the potential begins to rise slowly and stabilize during the test as a consequence of the reformation and thickening of the passive film on the electrode surface. However, The OCP trend of the as-printed condition changed erratically over the exposure time, whereas the ground sample was more stable; this observation indicates a dissolution dominant in the current



**Fig. 8 – KAM results for the (a) as-printed, (b) laser polished, and (c) shot peened samples.**





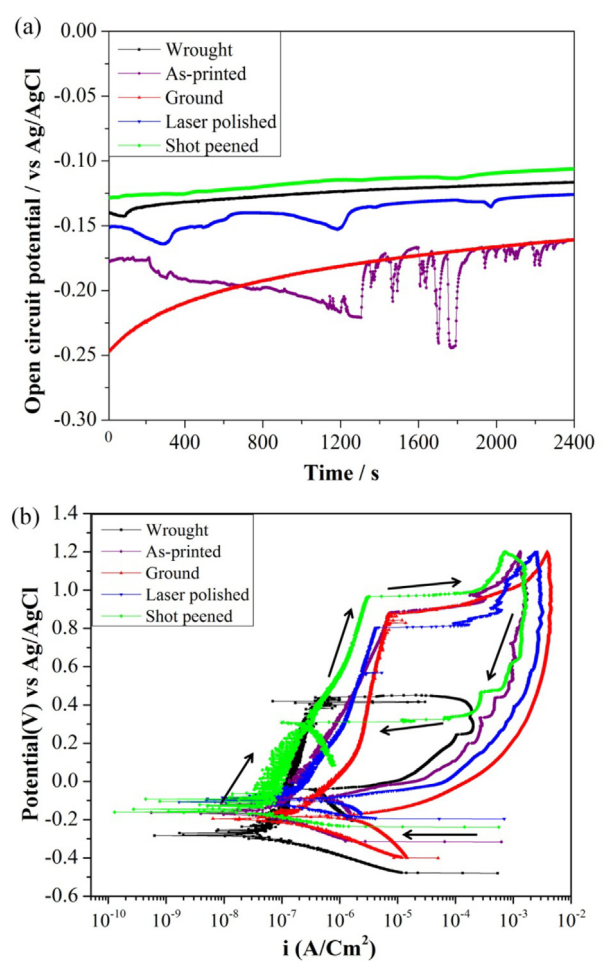
**Fig. 9 – Average top surface microhardness of the studied samples.**

condition as a consequence of high surface roughness for the as-printed sample (Fig. 3, Table 2).

Fig. 10(b) shows the cyclic potentiodynamic polarization curves of the as-printed and post-processed samples in a 0.9% NaCl solution. The polarization direction is indicated by black arrows in the plots. This method was used to determine the passive current density ( $I_{pass}$ ), corrosion potential ( $E_{corr}$ ), pitting potential ( $E_{pit}$ ), and repassivation potential ( $E_{rep}$ ) of the samples. Both  $I_{pass}$  and  $E_{corr}$  provide information on the interaction between the protective alloy surface and the corroding environment.

According to Fig. 10, the variation of the anodic polarization curve due to the surface post-treatment can be linked to the differences in surface properties, including roughness, crystal defects, and residual stress [21–23]. The electrochemical responses for the as-printed, post-processed, and wrought AISI316L samples in 0.9% NaCl solution are summarized in Table 3.

As seen in Table 3, the measured  $I_{pass}$  were  $0.341 \mu A/cm^2$ ,  $1.162 \mu A/cm^2$ ,  $0.324 \mu A/cm^2$  and  $0.113 \mu A/cm^2$  for the as-printed, ground, laser polished and shot peened AISI316L samples, respectively. The  $E_{corr}$  values varied from  $-0.245 V_{Ag/AgCl}$  (for the wrought sample) to  $-0.122 V_{Ag/AgCl}$  (for the shot peened sample). The apparent differences in corrosion behavior between the AM samples (as-printed and ground) and conventional wrought austenitic stainless steels can be primarily attributed to their different microstructural features [54]. The enlarged passivity of the as-printed and ground samples compared to the wrought sample could result from a more stable native oxide film [55]. Generally, AM austenitic stainless steels with minimal porosity exhibit better passivity



**Fig. 10 – (a) Open circuit potential measurements, (b) Cyclic potentiodynamic polarization curves for all samples in 0.9% NaCl.**

than their conventionally produced counterparts. Sander et al. [17] reported that in the case of an as-built AISI316L with a density over 99%, the resistance to pitting is generally increased compared to a conventionally made sample, thanks to the absence of MnS inclusions that reportedly act as the preferential sites for pit initiation. In conventionally-produced AISI316L samples, the dissolution of MnS inclusions is the most probable mechanism responsible for pit initiation, resulting in an aggressive local environment. Similar results were achieved in this work (Fig. 10).

However, surface roughness as an inherent characteristic of AM parts is one of the key parameters in determining their corrosion behavior since a rougher surface accelerates the electrochemical reactions between the surface and its immediate environment, leading to both general and localized

**Table 2 – Surface modifications for as-printed and post processed samples.**

	Sa, Sz ( $\mu m$ )	RS (MPa)	HV (25 g)	$F_{LAGB}, F_{HAGB}$	Total GBL (mm)
As-printed	14.11, 240.19	30	218	0.65, 0.34	2.29
Ground	0.51, 17.44	-95	225	-	-
Laser polished	1.09, 22.25	55	208	0.35, 0.65	1.82
Shot peened	1.66, 58.52	-240	286	0.77, 0.23	12.71

**Table 3 – Summary of electrochemical parameters obtained in 0.9% NaCl environment.**

Sample	$I_{\text{pass}}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{\text{corr}}$ ( $V_{\text{Ag}/\text{AgCl}}$ )	$E_{\text{pit}}$ ( $V_{\text{Ag}/\text{AgCl}}$ )	$E_{\text{rep}}$ ( $V_{\text{Ag}/\text{AgCl}}$ )	$E_{\text{pit}} - E_{\text{rep}}$ ( $V_{\text{Ag}/\text{AgCl}}$ )
As-printed	$0.341 \pm 0.055$	$-0.168 \pm 0.029$	$0.84 \pm 0.17$	$-0.09 \pm 0.02$	$0.93 \pm 0.09$
Ground	$1.162 \pm 0.078$	$-0.174 \pm 0.012$	$0.89 \pm 0.21$	$-0.18 \pm 0.03$	$1.07 \pm 0.12$
Laser polished	$0.324 \pm 0.071$	$-0.192 \pm 0.033$	$0.78 \pm 0.16$	$-0.09 \pm 0.07$	$0.87 \pm 0.11$
Shot peened	$0.113 \pm 0.023$	$-0.122 \pm 0.019$	$0.96 \pm 0.08$	$0.31 \pm 0.06$	$0.65 \pm 0.07$
Wrought	$0.122 \pm 0.032$	$-0.245 \pm 0.022$	$0.43 \pm 0.11$	$-0.04 \pm 0.02$	$0.47 \pm 0.07$

corrosion [23]. Comparing the as-printed and ground samples in Fig. 10 and Table 4, it can be noticed that decreasing the roughness of the surface lowers the electrochemical reactions, leading to a decrease in both general and localized corrosion. Moreover, during the polarization tests of the as-printed and ground samples, several current spikes were detected at the high anodic potential for the as-printed samples, indicating a metastable pit formation. In other words, there was a pre-existing passive layer on the sidewalls of partially melted particles and pores, but this protective layer was not stable enough and collapsed at higher anodic potentials causing fluctuations in the anodic branch of the polarization curve. Similar results were reported by other researchers working on the effect of surface roughness on the pitting resistance of AM AISI316L [33,34].

As shown in Fig. 10 and Table 3, the difference in  $I_{\text{pass}}$  value of the laser polished sample and as-printed one was minor. In addition, the corrosion potential ( $E_{\text{corr}}$ ) was slightly negative after laser polishing. These findings imply that the formation of a higher tensile residual stress and decrease in surface crystal defects are the primary causes of the slight deterioration of the corrosion behavior in the laser polished samples. In other words, the higher tensile stress in laser polished samples may result in the creation of corrosion cells inside the structure, with stressed zones serving as anodic areas leading to a minor increase in corrosion rate [15,56].

The surface of the shot peened sample was observed to be more reactive than the other surfaces due to the higher density of crystal defects (Fig. 6). Therefore, according to Fig. 10, the polarization curves for the shot peened sample are noisy when cathodic reactions are still occurring, with the passive plateau exhibiting a wavy form, demonstrating that even in the passive state, certain sites are still reactive. In general, the compressive residual stresses and higher density of crystal defects on the surface of the as-printed sample are the most significant variables affecting corrosion resistance and passive film generation. The high density of crystal defects, such as grain boundaries and dislocations, provide ample nucleation sites for passive film formation and subsequently influence the passive film properties. To enhance the corrosion properties of the AM AISI316L parts, grain refinement is

suggested by several researchers to improve the growth of the passive layer by decreasing the diffusion path length or, in other words increasing the diffusion rate for chromium atoms toward the surface to form a protective and homogeneous chromium oxide layer [37–40]. Overall, our findings are consistent with earlier research on the passive film characteristics of austenitic stainless steel showing the influence of grain size and residual stress levels [34,57–59].

The  $E_{\text{pit}}$  and  $E_{\text{rep}}$  mean values of the different samples as a function of roughness, residual stress, and grain boundary lengths of the individual samples are plotted in Fig. 11.

The  $E_{\text{pit}}$  values of all samples were found to be within the range 0.83–0.96  $V_{\text{Ag}/\text{AgCl}}$  (Table 3), which is about 400 mV higher than the  $E_{\text{pit}}$  of the wrought AISI316L sample. This behavior is related to the nature of the inclusions and their distribution within the microstructure, which commonly act as pit initiation sites on the metal surface and consequently decrease the susceptibility to pitting. Evidence of increased pitting corrosion values  $E_{\text{pit}}$  after post-treatment is provided by other researchers [21,30].

The formation of an unstable or thin passive film on a highly rough surface will eventually form steady-state pits and decrease the pitting potential [23,60,61]. It has also been demonstrated that the repassivation ability of the as-printed sample is relatively weaker than the ground samples, a behavior which is attributed to the surface roughness and partially melted particles on the surface (Fig. 11(a)). When the corrosive solution is confined in these regions, the chemistry of the solution alters, resulting in de-passivation and preventing the creation of a stable, uniform passive layer [21,22]. Also, defects such as partially melted particles, pores, and inclusions in the passive film (as-printed and wrought sample) trigger localized corrosion attacks through several mechanisms, like creating Cr-depleted regions or decreasing the repassivation ability of the alloy. On the other hand, the average  $E_{\text{rep}}$  for the shot peened sample was at least 0.32  $V_{\text{Ag}/\text{AgCl}}$ , which was above the average  $E_{\text{rep}}$  recorded for other samples.  $E_{\text{rep}}$  was found to decrease with sample surface tensile residual stress (Fig. 11(b)). In other words, repassivation after stable pitting, as triggered by anodic polarization, was more favored in samples with compressive residual

**Table 4 – Variations in the impedance parameters and passive film thickness of all samples in 0.9% NaCl.**

Sample	$R_s$ ( $\Omega \cdot \text{cm}^2$ )	$R_p$ ( $\text{k}\Omega \cdot \text{cm}^2$ )	CPE ( $\mu\text{F} \cdot \text{cm}^{-2}$ )	n	L (nm)
As-printed	$328.2 \pm 0.1$	$13.83 \pm 0.17$	$7.85 \pm 0.52$	$0.83 \pm 0.05$	1.8–2.1
Ground	$312.9 \pm 0.3$	$12.62 \pm 0.22$	$1.12 \pm 0.46$	$0.87 \pm 0.04$	2.4–2.7
Laser polished	$304.7 \pm 0.2$	$7.23 \pm 0.18$	$6.81 \pm 0.37$	$0.79 \pm 0.07$	2.2–2.5
Shot peened	$328.9 \pm 0.4$	$24.31 \pm 1.56$	$6.75 \pm 0.22$	$0.84 \pm 0.11$	3.6–3.9
Wrought	$308.3 \pm 0.7$	$5.04 \pm 1.32$	$1.48 \pm 0.72$	$0.82 \pm 0.08$	1.9–2.2

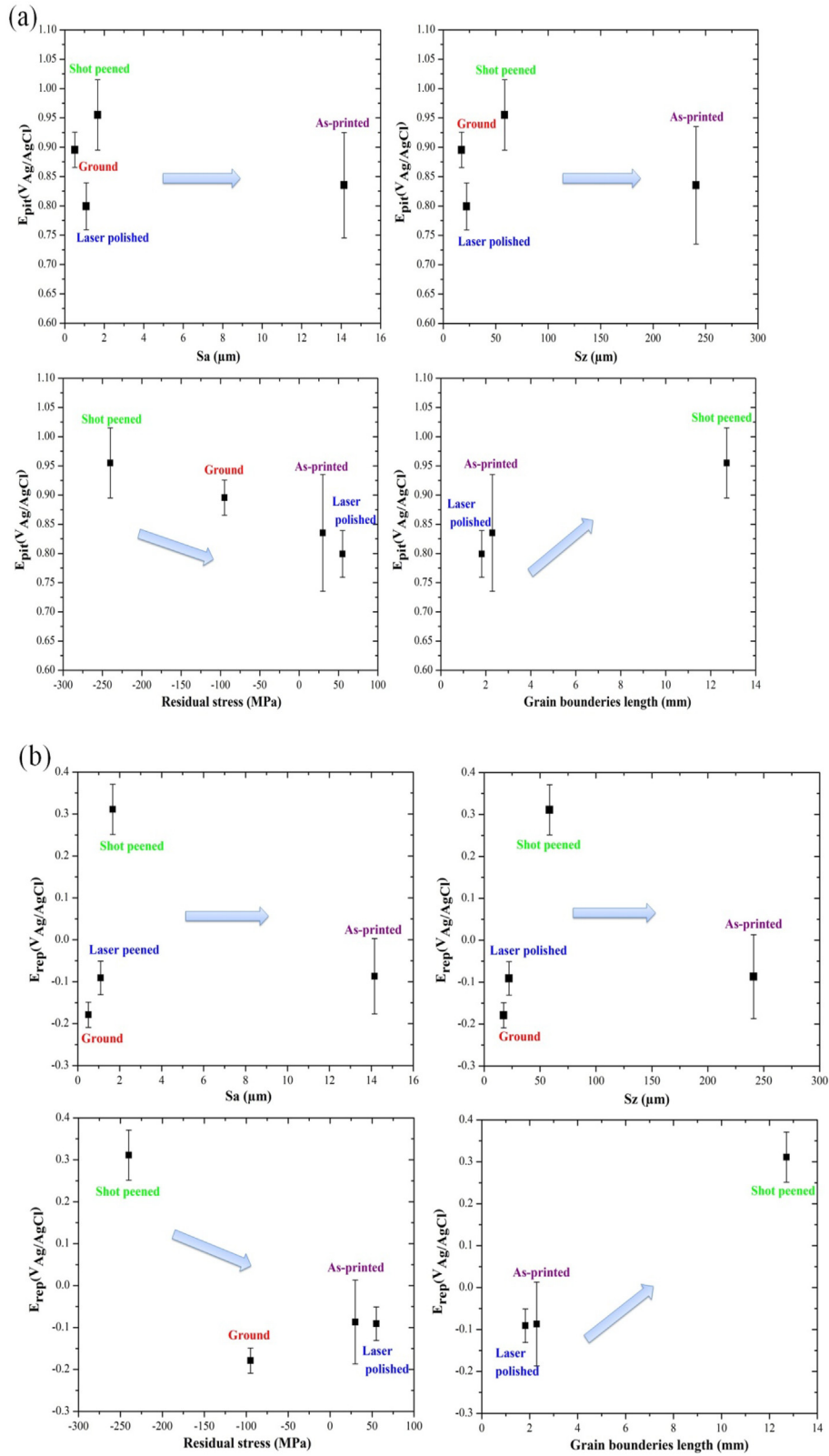


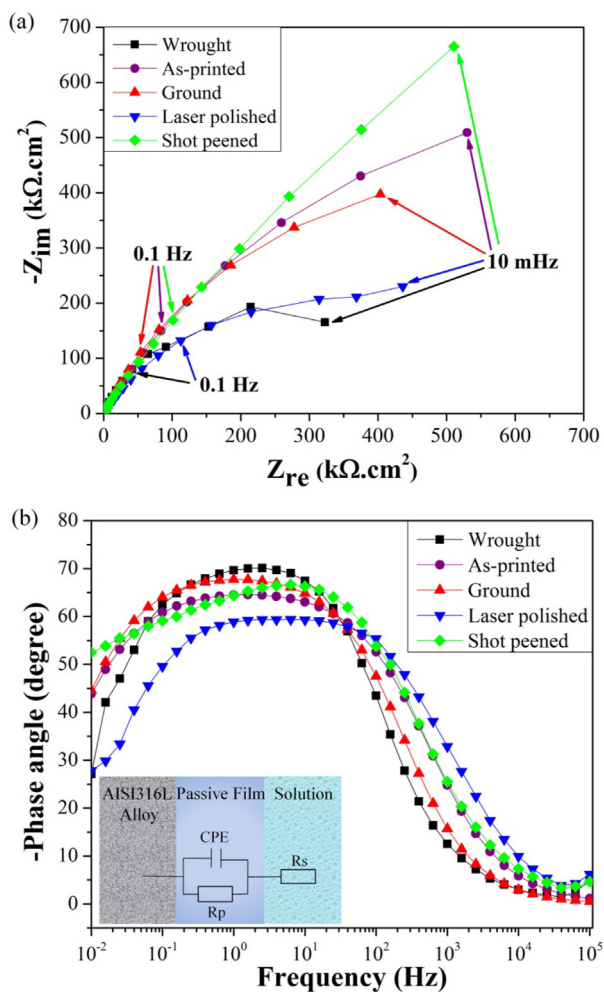
Fig. 11 – Relationships between (a) pitting potential and (b) repassivation potential as a function of surface roughness, residual stress, and grain boundaries length.

stress on the surface. All in all, it was observed that the shot peening treatment (Fig. 11(a and b)) induced more notable corrosion modifications compared to the other treatments. The significant improvements noticed for the shot peened samples can be due to the combined effect of a lower surface roughness with more regular surface morphology compared to the as-printed state along with compressive residual stress on the surface. In addition, formation of a high density of crystal defects on the surface may be considered as a positive factor influencing the corrosion behavior of the shot peened sample.

### 3.5. Electrochemical impedance spectroscopy tests

The EIS response of different samples in 0.9% NaCl solution was investigated at the open-circuit potential, and the results are shown as Nyquist and Bode-phase plots in Fig. 12. The experimental data are represented by symbol points, while the fitted data are represented by a straight line of the same color.

Based on the Nyquist plots (Fig. 12(a)), it can be pointed out that typical capacitive semi-loop shapes are similar for



**Fig. 12** – EIS plots for the as-printed and post-processed AISI316L samples: (a) Nyquist plots, (b) Bode plots (Inset shows the equivalent circuit used to fit the data).

all samples, while the diameters are different. The imperfect semicircle diameter for the shot peened sample was higher than that of other series, reflecting better passivation behavior and formation of stable oxide film on the surface of the shot peened sample. However, the roughness (as-printed vs. ground) and residual stress (as-printed vs. laser polished) had no significant effect on the stability of the passive film. Therefore, similar to the cyclic potentiodynamic polarization curves, the differences between the as-printed and ground parts are rather low. More specifically, as seen in Fig. 12 (b), the Bode-phase curves show one time constant (only one maximum phase angle at the middle frequency range). It seems that at or near OCP, the mechanism of corrosion reaction for all samples was the same and mainly controlled by the charge transfer phenomena through the protective layer. Also, the constant phase nature of the impedance at low frequencies is a consequence of defect transport within the oxide film, mainly due to the migration of metal ions and vacancies under the influence of the electric field. Hence, the phase angle values remained very close to  $-75^\circ$ , revealing the formation and growth of a passive film for all samples. Moreover, to simulate the measured impedance data, a simple circuit (Fig. 10(c)) comprising of solution resistance ( $R_s$ ), polarization resistance ( $R_p$ ), and constant phase element (CPE) was used for fitting the EIS data (Fig. 10(a)). It can be seen that the CPE is parallelly connected to an oxide film resistance ( $R_p$ ) and serially to the previous two components with a solution resistance ( $R_s$ ). The electrical impedance of CPE can be calculated by Eq. (1) [34]:

$$Z_{CPE} = \frac{1}{Q(\omega j)^n} \quad (1)$$

where  $Q$ ,  $\omega$ ,  $n$ , and  $j$  are constant, angular frequency, capacitor coefficient behavior and the imaginary factor, respectively. The factor  $n$  is the dispersion index, and the value of  $n$  indicates the deviation from the pure capacitor where  $n = 1$ . The variation of the impedance parameters obtained from fitting the EIS data of the wrought, as-printed, and post-processed samples in a 0.9% NaCl solution is illustrated in Table 4.

According to the EIS results, the shot peened sample exhibited better barrier properties (higher polarization resistance). This enhanced passivity for the shot peened sample can be attributed to residual stress and crystal defects due to the mechanical treatment. In other words, it is suggested that the construction and growth of the passive film may be modified by increased lattice defects and compressive stress levels in the substrate. Indeed, the residual stress changes the inter-atomic distance, and a narrower inter-atomic distance obtained by compressive residual stress increases the probability of the presence of Cr atoms at the metal/environment interface AISI316L sample. This phenomenon leading to prevent the migration of point defects across the passive film and the formation of passive film enriched in Cr-oxides [57]. However, according to the results obtained for the as-printed sample compared to the laser polished or ground samples, it seems that the residual stress at or near OCP has no significant effect on the polarization resistance and stability of the passive film. Similar results were also reported by Cruz et al. [34], where L-PBF AISI316L samples with different residual stress



levels had similar charge transfer resistances as the as-built sample. On the other hand, an increase in the density of crystal defects such as dislocations and grain boundaries (Fig. 8(c)) promotes the diffusion of passivating elements (like Cr) towards the surface, enabling the rapid formation of a homogeneous, thicker, Cr-enriched, and compact passive film. To elaborate this behavior, the variation of the passive film thickness ( $L_{ss}$ ) of the studied samples were calculated using the following Eq. (2) [62]:

$$L_{ss} = \frac{\epsilon \epsilon_0 A}{C_f} \quad (2)$$

where  $\epsilon_0$  is the vacuum permittivity ( $8.854 \times 10^{-14} \text{ Fcm}^{-1}$ ),  $\epsilon$  is the dielectric constant for the passive film (15.6 for stainless steel [34,63,64]),  $A$  is the effective area of the electrode, and  $C_f$  is the total capacitance of the passive film measured from the EIS results, after the formation of the oxide film [65]. This equation demonstrates that any change in the total capacitance of the passive film is indicative of variation in the passive film thickness. In other words, an inverse relationship between capacitance and the thickness of the passive film was noticed in this investigation, whereby grain refinement was more effective than the surface roughness and residual stress. The total capacitance of the passive film is obtained from Eq. (3) [66]:

$$C = -\frac{1}{2\pi f Z''} \quad (3)$$

where  $Z''$  is the imaginary component of the impedance and  $f$  is the frequency. The 1000 Hz is used in this study. The calculated values for  $L$  are shown in Table 4, which are in agreement with the previous studies [55,67].

Therefore, surface mechanical post-treatment, simultaneously inducing crystal defects, compressive residual stress, and work hardening, facilitate the formation of a thicker passive film that seems to be the most pertinent factor behind the corrosion resistant improvement against passive layer rupture.

### 3.6. Mott-Schottky analysis

Generally, oxide films with perfect crystal structures can be considered as insulators. However, the presence of point defects in the passive films, such as oxygen vacancies and cation interstitials, can make them behave as extrinsic semiconductors when exposed to an aqueous solution. Indeed, the physico-chemical properties of the passive films are dominated by the point defects motion and distribution, which are responsible for the passive film's steady state. Mott–Schottky analysis has been employed to determine the semiconductor type and dopant density of the passive film [64,65,68].

According to the Mott–Schottky theory, the space charge capacitances (CSC) of n-type and p-type semiconductors can be calculated by Eqs. (4) and (5), respectively:

$$\frac{1}{C_{sc}^2} = \frac{2}{e\epsilon\epsilon_0 N_D} \left( E - E_{fb} - \frac{k_B T}{e} \right) \quad (4)$$

$$\frac{1}{C_{sc}^2} = -\frac{2}{e\epsilon\epsilon_0 N_A} \left( E - E_{fb} - \frac{k_B T}{e} \right) \quad (5)$$

where  $e$  is the electron charge ( $1.6 \times 10^{-19} \text{ C}$ ),  $N_D$  and  $N_A$  are the donor and acceptor density ( $\text{cm}^{-3}$ ), respectively. The variables  $E$ ,  $E_{fb}$ ,  $k_B$ ,  $T$  are the applied potential (in  $V_{Ag/AgCl}$ ), flat band potential (in  $V_{Ag/AgCl}$ ), and the Boltzmann's constant and absolute temperature, respectively. Fig. 13 represents the electrode capacitance versus applied potential plots for a passive film formed on the as-printed and post-processed samples in a 0.9% NaCl solution. All plots reveal two linear parts indicating the Mott–Schottky-type (n-type and p-type semiconductor) behavior. As depicted in Fig. 13, the passive film capacitance is lower for the shot peened sample compared to the ground and as-printed ones, all having lower capacitance with respect to the laser polished sample. This decrement in the passive film capacitance suggests lower dissolution and an increase in the passivity of the shot peened samples compared to the other series.

As shown in Fig. 13, positive slopes within the potential range  $-400$  to  $+100 \text{ mV}_{Ag/AgCl}$  indicate n-type semiconductor behavior of passive film formed on all the L-PBF AISI316L samples [34,65,69,70]. From the linear part of the plot, the donor density of the passive layer can be estimated using Eq. (6):

$$N_d = \frac{2}{e\epsilon\epsilon_0 a} \quad (6)$$

where  $a$  is the slope in n-type region. The donor density calculated with this method indicates the density close to the passive film/alloy interface, which is directly related to the concentration of point defects in the passive film, such as oxygen vacancies or metal interstitials in an n-type semiconducting oxide layer [65,71]. The donor density values for the passive films formed on all the samples are plotted as a function of the surface roughness, residual stress and grain boundaries length in Fig. 14. For all the samples, the density is about  $10^{20} \text{ cm}^{-3}$ , which is in excellent agreement with the data reported in the literature [67,72,73].

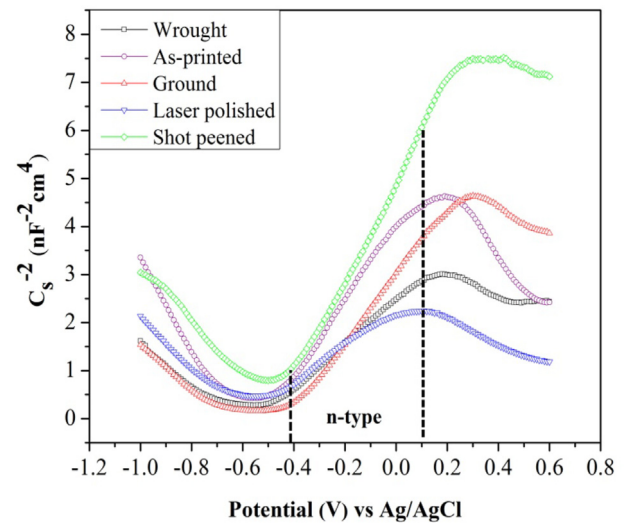


Fig. 13 – Mott-Schottky curves at frequency 1 kHz measured in the cathodic direction for all samples in 0.9% NaCl.

According to Fig. 14, almost similar results were obtained for the as-printed and ground samples. However, the donor density of the passive film formed on the shot peened sample was less than that of the as-printed sample, which reflected better passivation behavior of the shot peened sample. In other words, the number of point defects was decreased in the passive film formed on the shot peened sample, while the as-printed sample exhibited a highly defective passive film. On the other hand, for the laser polished sample, a lower roughness and a higher tensile residual stress led to a slight decrease in the donor density and point defect concentration within the passive film, as compared to the as-printed sample. Generally, a higher donor density value indicates a higher conductivity and lower oxide film quality with n-type semiconductive properties [69]. Moreover, based on the point defect model (PDM) [65,71,74], the above results show that the donor density and electrostatic field within the passive film are affected by surface roughness, crystal defect density, and the state of the residual stress on the surface. Overall, it was noticed that by increasing the crystal defects such as grain boundaries and dislocations, known as rapid path diffusion of elements, and inducing compressive residual stress, the kinetics of the interfacial reactions at the metal/film (generation of oxygen vacancies), film/solution interfaces (annihilation of oxygen vacancies), and also within the passive film became faster. This phenomenon led to the formation of a denser

passive film on the shot peened sample compared to the other samples, demonstrating an improved electrochemical response. Therefore, it should be noted that the high density crystal defects generated a passive film containing richer Cr by promoting the Cr diffusion towards the surface, which may strengthen the passive film [23,64].

Considering the obtained results, it can be concluded from Fig. 15 that the lower pitting potential of the as-printed sample, compared to the ground and shot peened ones (Table 3), was mainly attributed to the increased donor density and point defect concentration of the passive film. Overall, crystal defects and compressive residual stresses decrease the donor density within the passive film, eventually affecting the pitting nucleation and metastable pitting process and reducing the transition probability from the metastable pitting to the stable pitting. Therefore, the lower the defect densities, the higher the pitting corrosion resistance.

Schematic representations of the effect of different post-treatments on sample's behavior after immersion in a corrosion environment at room temperature are shown in Fig. 16. Various parameters such as roughness, crystal defects, work hardened zone, residual stress, and corrosion characteristics discussed in the previous sections are detailed on these diagrams.

The surface of the as-printed sample is rough and under tensile residual stress in Fig. 16(a), but the surfaces of ground

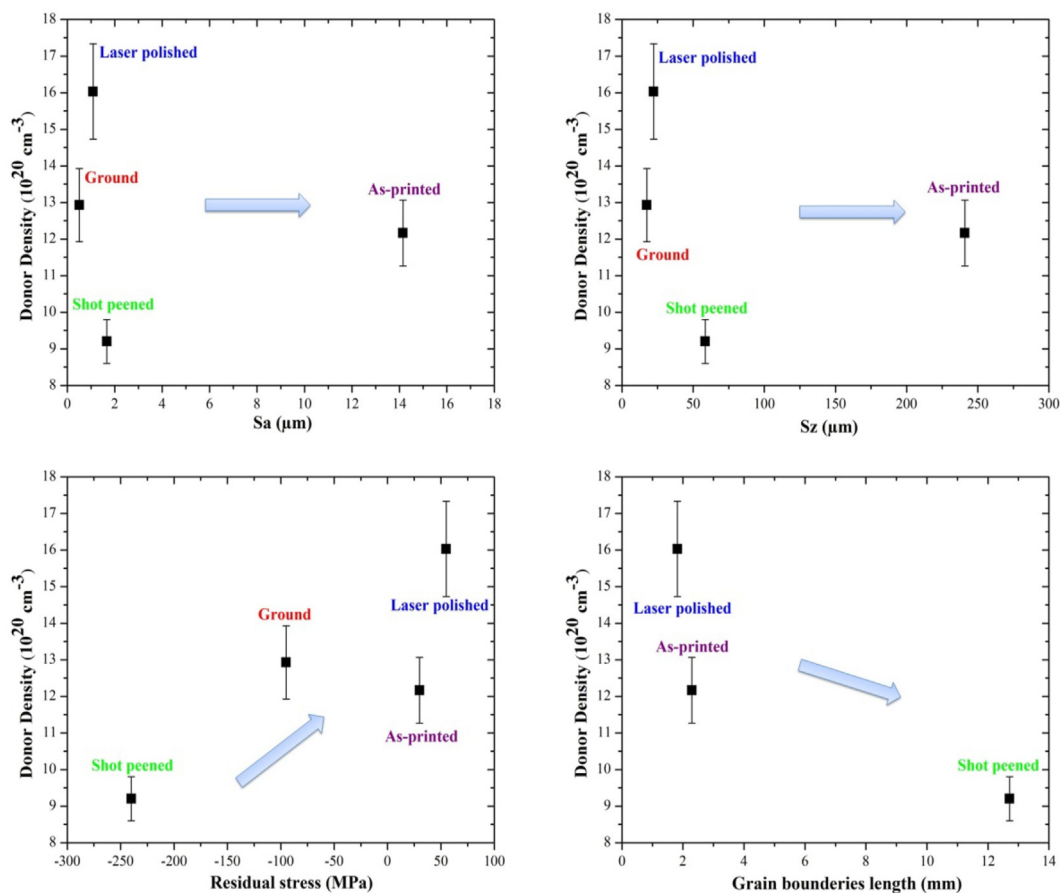
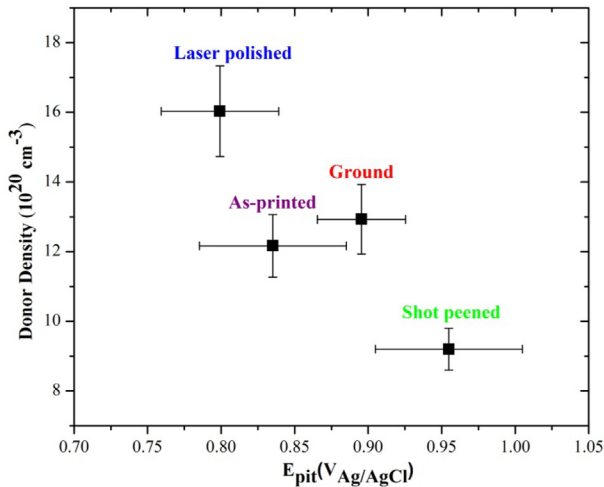


Fig. 14 – Relationship between donor density as a function of surface roughness, residual stress and grain boundaries length.

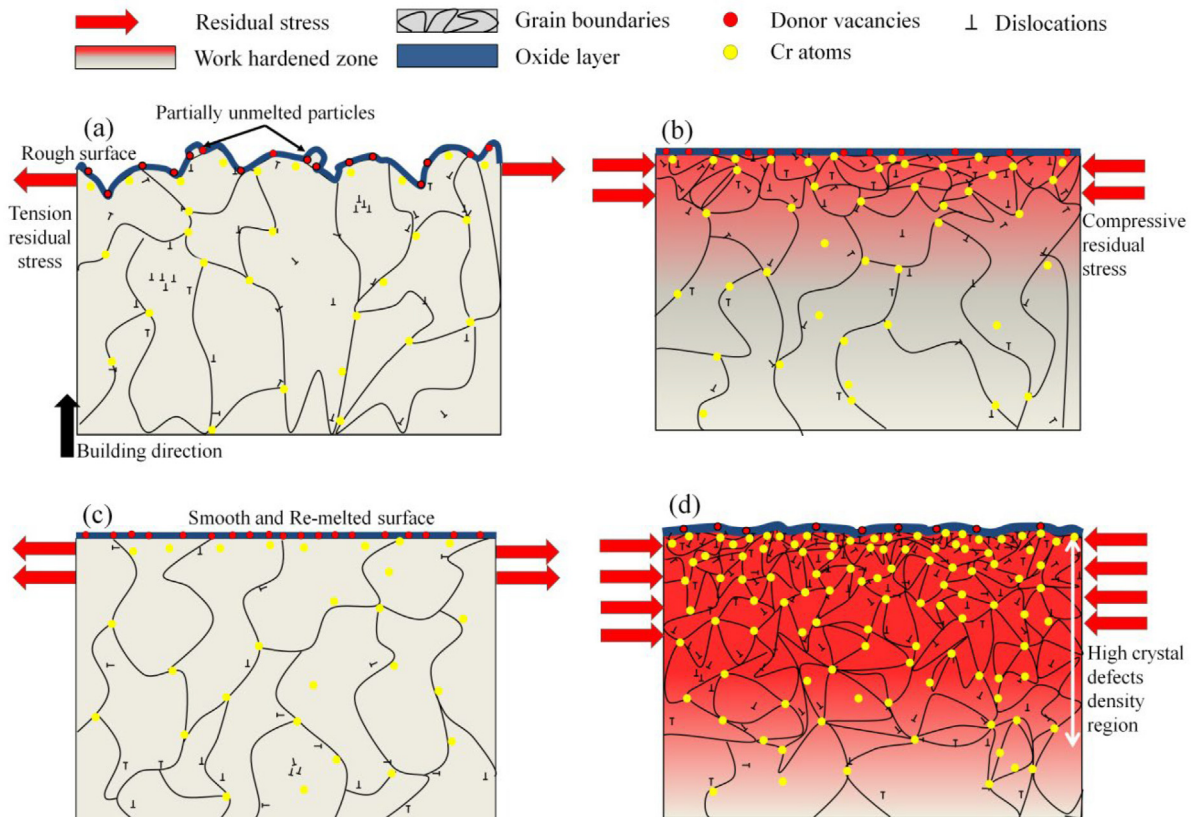


**Fig. 15 – Relationship between donor density and pitting potential for the as-printed and post treated samples.**

and shot peened samples (Fig. 16(b) and (d)) are smoother and under compressive residual stress. Moreover, the surface of the laser polished sample, shown in Fig. 16(c), featured low surface roughness and high tensile stress, unlike the other samples. However, from the crystal defects point of view, the shot peened surface exhibited a high density of crystal defects due to the plastic deformation and work hardening effect (Fig. 7 and Table 2).

As a passive film grows on all the surfaces, each previous factor can affect all the elementary processes associated with corrosion, i.e., charge transfer, film defects, film growth, and film stability. Indeed, these modifications have an impact on the current densities, the existence of the passive state and the occurrence of pitting [67,69,71,75]. It is reported that the stress level and lattice microstrain (that are directly related to KAM (Fig. 8) and microhardness (Fig. 9) values) are inversely proportional to interatomic distances at the metal surface [23,57,76]. Hence, it would be reasonable to assume that samples with higher KAM values (Fig. 8) have a higher atomic density at the surface. Moreover, higher compressive residual stress that is directly relevant to higher microstrain could reduce the required activation energy for the dissolution of atoms at metal/solution interfaces [40,76]. In the meantime, increasing crystal defect density (i.e., grain boundaries and dislocations) induced by plastic deformation promotes atomic diffusion in the upper-most subsurface zones and increases nucleation sites for the growth of the passive film. Hence, more available metal ions and nucleation sites facilitate the creation of a denser passive layer, including less point defect concentrations and consequently affect the corrosion prosperities [40,77,78].

Therefore, in terms of the metallurgical state of the surface, after the samples are immersed in corrosion media, as-printed sample is characterized by a very high donor density and a thin film (Fig. 13 and Table 3), which is grown on a rough surface with tensile residual stress. The edge effect probably



**Fig. 16 – Schematics of surface modifications and passive film formation on the surface of (a) as-printed, (b) ground, (c) laser polished, and (d) shot peened samples.**

promotes the injection of point defects thanks to the rough surface created in the as-printed sample [79]. However, the passive film formed on the ground surface is thicker, with a lower doping density and almost no roughness, having compressive residual stress. On the other hand, the passive film thickness formed on the laser polished surface is higher than a disordered surface (as-printed) because the surface becomes smooth, and the passive layer tends to become more stable. Finally, the passive film formed on the shot peened surface is the thickest, with the lowest doping density among all other samples. The lower surface roughness of shot peened series, the compressive residual stresses and the higher density of crystal defects such as grain boundaries and dislocations caused by surface plastic deformation that enhance the reactivity of the surface, play essential roles in the passive film properties of metallic AM samples.

#### 4. Conclusions

The present study investigated the corrosion behavior of AISI316L samples produced via laser powder bed fusion AM method before and after different surface post-treatments including grinding, laser polishing and shot peening; the results were compared with those of a wrought sample. The main conclusions can be summarized as follow.

- 1 Based on the results obtained from EBSD analysis, grain boundary lengths and dislocation density on the surface of the shot peened samples were remarkably higher than the other series. This promoted surface hardness and induced compressive residual stresses on the surface. However, for the laser polished sample, the density of low angle grain boundaries was markedly reduced as a consequence of thermal input during the remelting process, where the dislocations were annihilated.
- 2 Electrochemical examinations demonstrated an increased pitting potential (mainly after shot peening) due to the high lattice defects density and large compressive stresses, which play an important role in reducing pit formation. The  $E_{\text{pit}}$  values were found to increase while  $E_{\text{pit}} - E_{\text{rep}}$  values were also decreased by the increase of crystal defect density and compressive residual stress.
- 3 According to the EIS results, there was no significant difference in the electrochemical impedance and stability of the passive films formed on the as-printed, ground and laser polished samples. However, significant differences were observed in the polarization resistance ( $R_p$ ) of the oxide layer of the shot peened samples, suggesting that the crystal defects of passive alloys could affect the passivation process by changing the element's diffusion rate. Moreover, the film grown on the shot peened sample was slightly thicker than the other samples.
- 4 Based on the point defect model and Mott-Schottky analysis, it is hypothesized that induced compressive residual stress and increased crystal defect density on the sample surface induced by shot peening could increase the resistance of the passive layer against defect transport and pit initiation. The modifications of the surface properties with the peening-based mechanical treatment lowered the

donor density and point defect concentration in the passive film.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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