Enhanced electrochemical corrosion resistance of 316L stainless steel manufactured by ultrasonic rolling assisted laser directed energy deposition

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Abstract: Under the laser directed energy deposition (LDED) process, the rapid melting and solidification usually lead to the emergence of pores and coarse columnar dendrites, which in turn compromise the properties of the deposited alloys. This study introduced in-situ ultrasonic rolling (UR) as an innovative method to enhance the corrosion resistance of LDED specimens, and the microstructural characteristics and their correlation with corrosion resistance were deeply investigated. The findings reveal that the LDED-UR specimen exhibits a reduction in both the fraction and size of pores. Under the influence of severe plastic deformation generated by LDED-UR process, fully equiaxed grains appear with a reduced average size of 28.61 μ m (compared to 63.98 μ m for the LDED specimen with columnar grains). The electrochemical corrosion resistance of the LDED-UR specimen is significantly enhanced compared to the LDED specimen. This enhanced corrosion resistance can be attributed to the low fraction of small-sized pores, the fine and uniformly distributed Cr-enriched ferrite phase, and the formation of a compact and thick passive film due to dense grain boundaries. The insight of the correlation between microstructure and corrosion behavior opens up a new pathway to enhance the corrosion resistance of LDED specimens.

Keywords: laser directed energy deposition; ultrasonic rolling; 316L stainless steel; microstructure; electrochemical corrosion resistance

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1 Introduction

Due to their exceptional tensile strength and corrosion resistance, 316L stainless steel has been extensively used in a variety of industrial sectors, such as marine infrastructure and transportation^[1, 2]. Moreover, the enhanced mechanical properties and corrosion resistance of this stainless steel make it a promising candidate for next-generation materials in the aerospace

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industry ^[3, 4]. However, the intricate structure of components presents increased challenges and costs in the traditional manufacturing process, particularly for customized components ^[5, 6]. Therefore, there is a growth demand for innovative manufacturing methods within these industries.

Laser directed energy deposition (LDED), a pioneering 3D manufacturing technology that utilizes the high energy of lasers to melt powders or wires to manufacture components, has gained wide attention from researchers ^[7-10]. Huang et al. ^[11] elucidated the pore formation mechanisms, highlighting that these pores can diminish the service lifespan of deposited components. Liu et al. ^[12-14] observed that the deposited alloy exhibited nonuniformly distributed microstructures due to the repeated heating and cooling cycles. Concurrently, LDED technology has also been employed by some researchers to manufacture 316L stainless steel ^[15, 16]. Su et al. ^[17] introduced the proportional integral

derivative control method to eliminate pores formed during the LDED process, and claimed that the forming quality is significantly enhanced through real-time modulation of laser power. Despite numerous endeavors to augment the properties of components fabricated by LDED, the persistence of pores and undesirable coarse dendrites remains a critical obstacle, impeding the widespread acceptance of LDED technology for load-bearing components. Therefore, innovative strategies are imperative to address these challenges.

Researchers have developed a variety of methods to address defects arising from additive manufacturing ^[18, 19]. Niu et al. ^[20] introduced an innovative BCC to FCC transformation strategy to inhibit cracking in additively manufactured high entropy alloys by adjusting the crystal structure. They discovered that poor grain deformation coordination is the primary cause of cracks, and their approach offers a novel solution in solving the cracks. Xu et al. ^[21] added ZrH₂ particles into AA7075 alloy and deposited a fine equiaxed grain alloy via LDED processing. They found that the resulting Al₃Zr particles act as heterogeneous nucleation sites, which refine the grains and enhance the mechanical properties of the additively manufactured aluminum alloy. The addition of other particles results in complex solidification condition of the melt pool under additive manufacturing, and the metallurgical defects such as cracks or pores appear easily. In this case, the incorporation of auxiliary fields has drawn the attention of scholars. Lu et al. [22] developed an in-situ micro-rolling assisted WAAM (wire arc additive manufacturing) method to fabricate the ultrahigh-strength steel AerMet100, and achieved deposited alloy samples with fine grains. Xie et al. ^[23] also found that the size and number of pores can be effectively reduced by micro-rolling assisted arc additive manufacturing. The refinement of grains and reduction of defects positively impact the enhancement of properties. Other methods, such as laser shock peening ^[24], ultrasonic vibration ^[25], electromagnetic field ^[26], etc., have been developed to reduce defects and improve the properties of deposited samples. Among these methods, the application of assisted plastic deformation on deposited layers is considered as an effective method in refining grains, eliminating defects, and ultimately enhancing the properties of alloys.

In challenging environments such as the ocean, electrochemical corrosion resistance is a critical performance criterion for 316L stainless steel components ^[27, 28]. Numerous researchers have endeavored to enhance the corrosion resistance of additively manufactured 316L stainless steel, and its associated corrosion behavior has been the subject of extensive studies. Li et al. ^[29] employed surface mechanical attrition treatments to induce gradient nanostructures on the surface layers, discovering that the corrosion resistance can be enhanced by reduced grain size and increased microstrain energy. Vukkum et al. ^[30] deposited 316L stainless steel by adding carbon nanotubes via laser power bed fusion technology, and discovered a decrease in the number of pits. This is primarily attributed to the refinement of Mn-Si-O nanoinclusions. Xu et al. [31] summarized that an appropriate heat treatment can enhance the corrosion resistance of the additively manufactured 316L stainless steel, which is consistent with the findings of Xiao et al.^[32]. For these suggested methods, altering the material composition will result in an increase in the complexity of alloy phases and may introduce unforeseen performance challenges, thereby complicating the validation process for the functionality of printed components. The subsequent heat treatment technique is not appropriate for large components, which may induce significant deformation. Additionally, grain growth can compromise the properties of the material. The in-situ plastic deformation method can induce the refinement of grains, while it shows little impact on the melt pool. Ultrasonic vibration directly influences the melt pool but its refining effect is weak. So, it is reasonable to predict that the combination of ultrasonic vibration and in-situ rolling has the potential to refine grains, eliminate defects, and ultimately enhance the properties of alloys.

Ultrasonic rolling, a kind of plastic deformation technique, yields grain refinement and defects elimination on the treated surfaces, contributing to improved corrosion resistance ^[33]. In this study, an ultrasonic rolling assisted laser directed energy deposition (LDED-UR) equipment was designed to reduce defects, refine grains, and subsequently enhance the corrosion resistance of alloys. Therefore, it is important to evaluate the electrochemical corrosion resistance of 316L stainless steel deposited by LDED-UR process. Additionally, it is vital to elucidate the relationship between the microstructure and the corresponding electrochemical corrosion behavior.

2 Materials and methods

2.1 Materials

The employed spherical feedstock with an average size of 60 μ m was the gas-atomized commercial 316L stainless steel powders (Avimetal Powder Metallurgy Technology Co., Ltd., China), and its SEM image is shown in Fig. 1. Meanwhile, the chemical compositions (wt.%) of the adopted powders is: 17.03 Cr, 10.64 Ni, 2.55 Mo, 0.45 Mn, 0.11 Si, 0.024 C, and



Fig. 1: SEM image of the metal powders

balance Fe. Before the LDED, powders and substrate were both pretreated. The employed powders were dried at 100 °C for 12 h in a drying equipment. The substrate surface of 316L stainless steel plate with the thickness of 16 mm was grounded by #1000 and #1500 sandpapers to remove the oxide scale and then cleaned by deionized water. Furthermore, 99.99% Ar gas was employed during the deposition process to inhibit the oxidation of the deposited layers.

2.2 LDED-UR process

Figure 2 depicts the device utilized in the LDED-UR process. The LDED-UR system is an integration of two primary components: the LDED system and the UR system. The two components are affixed through L-shaped brackets to realize in-situ fabricating. The UR system [Fig. 2(b)] mainly consists of three elements, i.e., a roller, an ultrasonic horn, and an ultrasonic transducer. The roller was engineered to manipulate the deposited layers to obtain the densified equaxied microstructures. The ultrasonic transducer was employed to generate the mechanical vibration by converting ultrasonic signals. The generated mechanical vibration was amplified and transmitted by the ultrasonic horn to the roller. The vibration amplitude of the roller can be modulated by changing the ultrasonic power. Moreover, the distance between the laser focal point and the roller can be adjusted by changing the fixed height and rotation angle of the developed ultrasonic rolling equipment. A block of 90 mm×60 mm was deposited, as presented in Fig. 2(c). Figure 2(d) demonstrates the deposition process during LDED-UR process. Furthermore, the laser scanning direction is presented in Fig. 2(e).

The LDED and LDED-UR parameters employed in this study are displayed in Table 1. It is important to note that the listed values are the optimized parameters, which are derived from an extensive series of optimization experiments. Meanwhile, the optimization process was not analyzed in this study. For the LDED experiments, the ultrasonic rolling components was disassembled.

2.3 Microstructure characterization

The optical microscopy (OM) system was employed to analyze the defects and microstructure of LDED and LDED-UR specimens. Before conducting OM observation experiments, the specimens were ground by #800 to #3000 SiC sandpapers, followed by polishing with diamond suspension and colloidal silica suspension. Subsequently, the polished surfaces were etched using aqua regia solution (a mixture of 30 mL HCl and 10 mL HNO₃) for 20 s. Finally, the specimens were cleaned

Table 1: LDED and LDED-UR parameters utilized in this study

Parameters	Values
Laser power (W)	1,400
Laser scanning speed (mm·s ⁻¹)	8
Powder feeding rate (g·min ⁻¹)	8
Diameter of the laser spot (mm)	3
Layer thickness (mm)	0.3
Flow rate of the shielding gas (L·min ⁻¹)	1
Distance between laser spot and rolling point (mm)	15
Ultrasonic power (W)	600
Ultrasonic frequency (kHz)	20
Vibration amplitude (µm)	2.3



Fig. 2: (a) LDED-UR equipment, (b) detailed structure of the ultrasonic rolling equipment, (c) schematic diagraph of deposited specimen, (d) LDED-UR process, (e) laser scanning direction

immediately using an ultrasonic cleaning equipment. It is important to note that the specimens for microstructural analysis were cut from the left rectangle (marked by dotted line) of the deposited specimens presented in Fig. 2(c). Additionally, specimens for detection of pores were not etched.

The scanning electron microscopy (SEM) system was used to identify the phases presented in the deposited specimen. Before the SEM analysis, the specimen surfaces were ground using SiC sandpaper ranging from #800 to #3000. Diamond suspension and colloidal silica suspension were then utilized to achieve a mirror-like finish. After that, the specimens were carefully cleaned with an ultrasonic cleaner using the anhydrous ethanol (purity \geq 99.9%). Finally, the specimens were dried by the cooling air. It is crucial to note that the SEM specimens were not etched. The phase compositions were characterized by the energy dispersive spectroscope (EDS) equipped in the employed SEM. Moreover, the SEM technique was employed to characterize the corrosion morphologies after electrochemical tests.

The EBSD experiments were conducted on a SEM operation (MIRA4 LMH) equipped with an EBSD system (NordlysMax2) to characterize the microstructures. Prior to the EBSD analysis, the specimens were ground and polished, and then they were electrolytically etched for 15 s using 10 mL HClO₄ and 40 mL C₂H₅OH. Furthermore, 20 kV accelerating voltage was employed in the EBSD experiments.

The X-ray photoelectron spectroscopy (XPS, SHIMADZU) analysis was taken to analyze the constitution of the passive film, which were formed at the open circuit potential (OCP) for 2 h in the 3.5wt.% NaCl solution. The employed X-ray source was Al K α (1,486.6 eV), and the test area was 700 µm×300 µm. The binding energy of reference peak (C1s) were calibrated to 284.8 eV. Meanwhile, the Avantage software was employed to analyze the obtained XPS spectra.

2.4 Electrochemical test

An electrochemical workstation (CHI660E) with a threeelectrode system was used to conduct the electrochemical tests: the working electrode was the manufactured LDED/LDED-UR specimen, the counter electrode was a platinum sheet with the sizes of 10 mm×10 mm, and the reference electrode was a saturated calomel electrode (SCE, 0.242 V vs standard hydrogen electrode). The backside of the working electrode was connected to a copper wire, and then they were pressed against in epoxy resin. The exposed area of the working electrode was 1 cm². The corroded surfaces were ground via #80 to #3000 sandpapers, and then cleaned with deionized water, and finally dried. All the electrochemical tests were carried out in 3.5wt.% NaCl solution, and the ambient temperature was about 25 °C.

The anodic potentiodynamic polarization tests were conducted in a positive direction from -0.4 V to +0.5 V with a rate of 2 mV·s⁻¹. Then, SEM technique was employed to characterize the corroded surface morphology. Prior to the electrochemistry impedance spectrum (EIS) tests, the specimens were polarized at -0.1 V_{SCE} for 5 min to remove the oxide films. Subsequently, potentiostatic passivation test was performed for 1 h to stabilize the open circuit potential (OCP). After that, EIS tests were carried out at the OCP with the frequency ranging from 100 kHz to 0.1 Hz, and the AG amplitude was 10 mV. The Zview software was used to analyze the EIS data. Utilizing the Tafel extrapolation method and ASTM-G102-89 standards, the corrosion current density (I_{corr}) was determined by the intersection of the corrosion potential (E_{corr}) line and the cathodic Tafel slopes (β_c) ^[34, 35]. Three parallel measurements were conducted for each case to assure a good repeatability. The specimens for electrochemical test were cut from the right rectangle (marked by dotted line) of the deposited specimens in Fig. 2(c).

3 Results

3.1 Microstructure of LDED and LDED-UR specimens

3.1.1 Analysis of microstructure and phase structure

Figure 3 displays the pore characteristics in various zones of the LDED and LDED-UR specimens. Pore characteristics from the top, middle, and bottom zones of the LDED specimen are shown in Figs. 3(a1-a3), while those of the LDED-UR specimens are depicted in Figs. 3(b1-b3). Several pores, indicated by blue arrows, are evident within the LDED specimen [Figs. 3(a1-a3)], with an average pore size of approximately 35.6 µm. The presence of these pores can be attributed to the instability of the keyhole tip during the LDED process ^[36, 37]. When ultrasonic rolling is applied, there is a notable reduction in porosity density, as presented in Figs. 3(b1-b3). The average pore size in the LDED-UR specimen is measured to be approximately 9.1 µm, which is much smaller than that observed in the LDED specimen. The reduced pore size and fraction in the LDED-UR specimen are primarily attributed to the metal flow induced by ultrasonic rolling, which facilitates the closure of pores. Under the severe metal flow, semi-solid metal continuously squeezes the space of pores, and eventually occupies the their position.

Figure 4 shows the SEM images and elemental composition of the LDED and LDED-UR specimens. As shown in Figs. 4(a) and (b), there are three distinct phases: the matrix phase (marked by black arrow), the spherical phase (marked by blue arrow), and the stripe phase (marked by yellow arrow). These findings are consistent with those reported by Wu et al. [38]. For the stripe phases under LDED processing, it can be detected that the size of them is slightly larger than that in the LDED-UR specimen, and the stripe phases are uniformly distributed in the LDED-UR specimen. Meanwhile, line scanning of the stripe phases was performed, and the results are illustrated in Fig. 4(c). The line scanning energy spectrum clearly shows the presence of Cr and Mo enrichment in stripe phases, while the element Ni is poor within the stripe phase. For the 316L stainless steel manufactured by LDED, austenite and ferrite are the predominant constituents [39]. Atamert and King [40] have indicated that elements Cr and Mo are the stabilizers for the ferritic phase. Therefore, it can be deduced that the stripe phase is ferrite, and the matrix phase is austenite. It is important to note that the fraction of ferrite is similar in the LDED and LDED-UR specimens. Additionally, numerous spherical phases precipitate in both specimens, as depicted in Figs. 4(a) and (b). From Figs. 4(a) and (b), it can be clearly seen that the average size of the spherical phases in the LDED specimen is larger than those in the LDED-UR specimen. Surface scanning analysis results of LDED specimen are illustrated in Figs. 4(e-f), demonstrating the spherical phase in Fig. 4(d) is the Si oxides. The formation of the SiO₂ is because that the raw material contains 0.11wt.% Si, and the affinity between elements O and Si is stronger than that between elements O and Fe, resulting in the silicon oxide is more prone to form during rapid cooling and solidification. Additionally, the carefully cleaning procedures for specimens address that the contamination is not come from the grinding process. This result is also consistent with the research results of Wu et al.^[38].

3.1.2 Grain morphology

Figure 5 displays the grain morphology of the deposited specimens under two studied cases (LDED and LDED-UR). Along the building direction, four representative zones were chosen to study the grain characteristics of both LDED and LDED-UR specimens, as presented in Figs. 5(a1-a3) and Figs. 5(b1-b3), respectively. These zones are highlighted within the blue boxes in Figs. 5(a) and (b). An inspection of



Fig. 3: Features of pores in different zones of LDED (a1-a3) and LDED-UR (b1-b3) specimens



Fig. 4: SEM images of LDED (a) and LDED-UR (b) specimens, elemental line scanning of the yellow line in Fig. 4(a) (c); SEM image of the spherical phase in LDED specimen (d), elemental surface scanning of Si (e) and O (f)

Fig. 5(a) reveals the presence of columnar and dendrite grains in the LDED specimen. In the various zones of the LDED specimen, there is only a subtle variance in grain structure, as depicted in Figs. 5(a1-a3). Along the building direction, the amounts of dendrites are increased. In contrast, the LDED-UR specimen exhibits fully equiaxed grains, as presented in Fig. 5(b). From the magnified views in Figs. 5(b1-b3), the size of equiaxed grains remains consistent along the building direction.

To further characterize the grain morphology, EBSD analysis was conducted, and the resulting inverse pole figure is presented in Fig. 6. The grain morphology shown in Fig. 6 aligns with the observations from Fig. 5. According to Fig. 6, the average grain size of the LDED specimen is about 63.98 μ m, and that of LDD-UR sample is about 28.61 μ m, which is significantly finer than that of the LDED specimen. This

demonstrates that the grain size can be greatly refined by the application of in-situ ultrasonic rolling, i.e., LDED-UR.

3.2 Electrochemical corrosion behavior

3.2.1 Polarization behavior

Figure 7 plots the polarization curves for both the LDED and LDED-UR specimens. It is evident that the potentiodynamic polarization curves of two alloys present similar shapes, suggesting that the two specimens possess similar electrochemical processes. In the anodic regions of both curves, the current density firstly increases rapidly, and then appear as a plateau, and finally increases quickly in response to the increased potential. The pitting potential (E_{pit}) refers to the potential where the current density presents a sudden increase. The results of electrochemical corrosion parameters are presented in Table 2.



Fig. 5: Grain morphology of LDED (a) and LDED-UR (b) specimens observed by OM. It should be noted that figures (a1-a3) and (b1-b3) are the enlarged images from figures (a) and (b), respectively



Fig. 6: EBSD grain orientation maps of LDED (a) and LDED-UR (b) specimens



Fig. 7: Polarization curves of the LDED and LDED-UR specimens

Table 2: Electrochemical corrosion parameters of the LDED and LDED-UR specimens

Processes	E_{corr} (V _{SCE})	\pmb{E}_{pit} (\pmb{V}_{SCE})	I _{corr} (A⋅cm ⁻²)
LDED	-0.123	0.275	3.72×10 ⁻⁷
LDED-UR	-0.093	0.428	1.58×10⁻ ⁷

In order to quantitatively evaluate the corrosion resistance of the two scenarios, the corrosion rate (CR) was calculated according to the Faraday's law^[41]:

$$CR = K \cdot \frac{M}{n} \cdot \frac{1}{\rho} \cdot I_{corr}$$
(1)

where *K* is a constant, and it is $3.27 \times 10^{-3} \text{ mm} \cdot \text{g} \cdot (\mu \text{A} \cdot \text{cm} \cdot \text{year})^{-1}$. *M* refers to the molar mass of the studied alloy, and its value

is 55.845 g·mol⁻¹. *n* stands for the valence, and it is 2·mol⁻¹. ρ is the density of the alloy. The density of the LDED alloy and LDED-UR alloy is calculated using Archimedes method to be 7.71 g·cm⁻³ and 7.86 g·cm⁻³, respectively. Thereby, the corrosion rate of the LDED and LDED-UR specimens is calculated to be 4.402 µm·year⁻¹ and 1.834 µm·year⁻¹, respectively. Based on these findings, it is summarized that the LDED-UR specimen exhibits superior corrosion resistance compared to the LDED specimen.

3.2.2 EIS analysis

EIS experiments were employed to analyze the relative stability of the passive films formed on the LDED and LDED-UR specimens. Figure 8 illustrates the EIS curves and the equivalent circuit of the electrochemical system. The EIS data are depicted as Nyquist plots and Bode plots, where the points in figures represent the test results and the lines refer to the fitted data. A similar shape of the Nyquist diagrams can be detected in Fig. 8(a), implying comparable passive mechanism of the LDED and LDED-UR specimens. Meanwhile, the shape of them can be identified by capacitance loop with different diameters. The capacitance loop' diameter of LDED-UR specimen is larger than that of the LDED specimen. The increased diameter of the capacitance loop for the LDED-UR specimen indicates a strong corrosion resistance. From the Bode plots [Fig. 8(b)], it can be seen that the impedance moduli of the LDED-UR specimen are larger than that of the LDED specimen within the low frequency zone, suggesting the formation of a compact and dense passive film. This can also be verified by the high phase angle exhibited by the LDED-UR



Fig. 8: EIS spectrum and equivalent circuit of electrochemical system: (a) Nyquist plots; (b-c) Bode plots; (d) equivalent circuit

specimen in Fig. 8(b). In Fig. 8(c), a linear zone with a slope nearing –1 is noticeable within the frequency range from 1 Hz to 1,000 Hz, indicating that the formed passive film possesses capacitive characteristics.

A double-layer equivalent circuit illustrated in Fig. 8(d) is proposed to model the EIS data and describe the electrochemical corrosion behavior. As illustrated in Fig. 8(d), the equivalent circuit contains a porous outer layer and a dense inner layer. In the proposed circuit, R_s , R_f , and R_{ct} represent the solution resistance, the diffusion resistance for ions through the outer layer (passive film layer), and the charge transfer resistance, respectively. Meanwhile, CPE_1 and CPE_2 are the capacitances of the outer layer and the double electrical layer, respectively. The expression of the impedance of CPE (Z_{CPE}) is presented as:

$$Z_{\rm CPE} = \left[Y_0 \left(wi \right)^n \right]^{-1} \tag{2}$$

where Y_0 and *n* refer to the magnitude and exponent of CPE, respectively (for the ideal capacitance, n=1; for the nonideal capacitance, 0.5 < n < 1). *w* stands for the angular frequency, and *i* refers to the imaginary number ($i^2=-1$). For the fitter circuit parameters, R_s is 8.561 $\Omega \cdot \text{cm}^2$ for LDED specimen and 8.115 $\Omega \cdot \text{cm}^2$ for LDED-UR specimen. R_f is 238.6 $\Omega \cdot \text{cm}^2$ for LDED specimen and 181.8 $\Omega \cdot \text{cm}^2$ for LDED-UR

specimen. R_{ct} is 4,972 $\Omega \cdot cm^2$ for LDED specimen and 2,4341 $\Omega \cdot cm^2$ for LDED-UR specimen. Meanwhile, the fitted circuit parameters of CPE under the two processes (LDED and LDED-UR) are listed in Table 3. Furthermore, the effective capacitances related to the CPE₁ and CPE₂ are measured, and their results are also provided in Table 3. The calculated expressions of CPE are described as ^[42]:

$$CPE_{1} = Y_{0}^{\frac{1}{n}} R_{f}^{\frac{1-n}{n}}$$
(3)

$$CPE_2 = Y_0^{\frac{1}{n}} \left(\frac{R_s R_{ct}}{R_s + R_{ct}} \right)^{\frac{1-n}{n}}$$
(4)

Based on Eqs. (3) and (4), the effective capacitances are calculated, and the results are illustrated in Table 3. As shown in Table 3, it is evident that the effective capacitance of the LDED-UR specimen is significantly lower than that of the LDED specimen. Furthermore, the double layer effective capacitance of the LDED-UR specimen is half less than that of the LEDE specimen. The $R_{\rm et}$ of the LDED-UR specimen sharply increases by 389% to 24,341 $\Omega \cdot {\rm cm}^2$ compared to that of the LDED specimen, suggesting the formation of a compact passive film on the LDED-UR specimen. This shows a good agreement with the enhanced corrosion resistance exhibited by the LDED-UR specimen.

Table 3: Fitted parameters of CPE for LDED and LDED-UR specimens

Processes	R _s (Ω·cm²)	Υ ₀₁ ×10 ⁻⁵ (Ω ⁻¹ ·cm ⁻² ·s ⁿ)	n 1	CPE₁ (µF·cm ⁻²)	R _f (Ω·cm²)	Υ ₀₂ ×10 ⁻⁵ (Ω ⁻¹ ·cm ⁻² ·s ⁿ)	n ₂	CPE₂ (µF·cm⁻²)	R _{ct} (Ω·cm²)
LDED	8.561	8.44	0.747	22.5	238.6	2.358	0.823	3.78	4,972
LDED-UR	8.115	5.84	0.792	17.7	181.8	1.153	0.821	1.53	24,341

3.2.3 Corrosion morphologies

The surface morphologies and corresponding XPS analysis of the LDED and LDED-UR specimens after potentiodynamic polarization experiments were used to further evaluate the electrochemical corrosion behaviors. Figure 9 shows the corrosion morphologies of the LDED and LDED-UR specimens after potentiodynamic polarization test. It can be observed in Fig. 9(a) that the LDED specimen is characterized by the presence of dense and expansive corrosion pits. In contrast, the LDED-UR specimen features fine corrosion pits with a less extent, as illustrated in Fig. 9(b). This distinction implies that the LDED-UR specimen possesses superior corrosion resistance.

In order to characterize the elemental compositions of the passive film, XPS analysis was conducted on the corroded surfaces. Figure 10 exhibits the typical XPS spectra of these passive films. It can be observed that the compositions of the passive film for both specimens are consistent, primarily consisting of the hydroxides and oxides of Fe and Cr. This also suggests that the chemical compositions of the passive films are the same for the two cases. Additionally, the atomic contents of elements present on the surfaces of the corroded specimens are listed in Table 4. According to Table 4, it is distinctly noted that the atomic content of element Cr in the entire passive film of LDED-UR specimen is higher than that of the LDED specimen. The increased content of element Cr enhances the protection ability of the passive film, and finally improve the corrosion resistance of the LDED-UR specimen.

Figure 11 presents the fitted diagrams of high-resolution spectra for Fe 2p, Cr 2p, Mo 3d, and O 1s, separately. From Fig. 11, the chemical states and contents of species within the passive films formed on specimens can be thoroughly discerned and analyzed. Figures 11(a-b) present Fe 2p XPS spectra of the passive film on 316L specimen manufactured by LDED and LDED-UR. It can be seen that the predominant Fe species in the passive film include Fe, Fe₃O₄, Fe₂O₃, FeOOH, and Fe(II) sat. Meanwhile, the relative fractions of Fe compounds in the passive film is displayed in Fig. 12. The relative fractions of Fe³⁺ in the LDED alloy is recorded as 16.88%, while it is lower in the LDED-UR alloy at 13.64%. The Fe species with Fe³⁺ composition are more stable. The high fraction of Fe species with Fe³⁺ implies that a large



Fig. 9: Corrosion morphologies of LDED (a) and LDED-UR (b) specimens after potentiodynamic polarization test



Fig. 10: Typical XPS spectra of passive film on LDED and LDED-UR specimens

Table 4: Atomic contents of elements on the surfaces of corroded specimens (%)

Processes	Fe 2p	Cr 2p	Mo 3d	Ni 2p	0 1s
LDED	16.27	7.03	0.59	2.33	51.27
LDED-UR	15.14	12.82	1.35	3.27	42.05

amount of iron is corroded, i.e., worse corrosion resistance of the specimen. Thus, it can be inferred that the high levels of Fe^{3+} in the LDED alloy suggest its inferior corrosion resistance compared to the LDED-UR specimen.

It is important to note that Cr element plays a vital role in the corrosion resistance of stainless steels ^[43]. It can be easily



Fig. 11: Fitted diagram of high-resolution Fe, Cr, Mo, and O XPS spectrum in the passive film of LDED (a, c, e, g) and LDED-UR (b, d, f, h) specimens

seen from Figs. 11(c-d) that three main Cr species within the passive film are detected, and they are Cr, Cr_2O_3 , and $Cr(OH)_3$. Among them, Cr_2O_3 and $Cr(OH)_3$ are the dominant compounds of Cr in the passive films of the studied specimen, which significantly influences the corrosion resistance of the manufactured alloy. The relative fractions of Cr compounds in the passive film are displayed, as illustrated in Fig. 13. Figure 13 demonstrates that the relative fraction of Cr^{3+} in the passive film of LDED-UR specimen is about 7.81%, which is higher than that of LDED specimen (4.01%). High fraction of Cr^{3+} effectively mitigates the aggressive impact of Cl⁻, thereby protecting the integrity of the passive film.

The Mo 3d XPS spectra of the passive films are also analyzed, as shown in Figs. 11(e-f). It can be seen that Mo, MoO_2 , and MoO_3 are identified as the predominant Mo species. It is suggested by Montemor et al. ^[44] that the diffusion activity of ions (Fe³⁺, Fe²⁺, and Cr³⁺) within the passive film can be reduced by the metallic Mo. Meanwhile, the increased fractions of Mo⁴⁺ (MoO₂) and Mo⁶⁺ (MoO₃) within the passive film significantly contribute to reducing the density of oxygen vacancy defects associated with the presence of Fe²⁺. Figure 14 illustrates the relative fractions of Mo compounds in the passive film. From Fig. 14, it can be seen that the relative fractions of Mo⁴⁺ (MoO₂) and Mo⁶⁺ (MoO₃) in the passive film of the LDED-UR specimen are larger than those of the LDED



Fig. 12: Relative fractions of Fe components in the passive film of LDED and LDED-UR specimens



Fig. 13: Relative fractions of Cr components in the passive film of LDED and LDED-UR specimens



Fig. 14: Relative fractions of Mo components in the passive film of LDED and LDED-UR specimens

specimen. This suggests that a high fraction of Mo, MoO_2 , and MoO_3 in the LDED-UR specimen results in a compact and dense passive film, which is indicative of enhanced corrosion resistance.

4 Discussion

4.1 Microstructural evolution mechanisms

Based on the above findings, the fraction and size of pores are significantly reduced by applying assisted in-situ ultrasonic rolling processing. Meanwhile, the uniformly distributed ferrites with small sizes are exhibited in the LDED-UR specimen. Additionally, fine equaixed grains are also observed. These microstructural features are attributed to the combined effects of ultrasonic vibration and the severe plastic deformation caused by roller. Prior to the action of roller, ultrasonic vibration plays a pivotal role in refining the grains. The combined effect of cavitation and acoustic streaming, generated by ultrasonic vibration, enhances the fluidity of the melt pool and the mushy zone. Accordingly, bubbles can ascend more readily and are effectively expelled from the melt pool, resulting in a substantial decrease in the pore fraction of the material processed by LDED-UR.

Simultaneously, under the combined effects of cavitation and acoustic streaming, numerous microbubbles are generated in the melt pool. As the sound pressure hits a critical level, these microbubbles swiftly expand and then abruptly collapse. This process generates substantial shockwave energy within the melt pool and the mushy zone, causing the fragmentation and detachment of columnar grains ^[45]. Then, the resulting fractured and dispersed dendrites act as new sites for the nucleation of equiaxed grains.

The substantial rolling pressure applied by the roller induces severe plastic deformation, which generates a high density of dislocations. Under the combined effects of the ultrasonic energy field, cyclic thermal field, and plastic deformation, a high density of dislocation emerges. These dislocations then rapidly glide and coalesce within a short period. The amalgamation of dislocations results in the formation of smallangle grain boundaries that progressively transform into new grain boundaries. This dynamic recrystallization process further contributes to the refinement of the grain size.

4.2 Electrochemical corrosion mechanisms

To better elucidate the strengthening mechanisms of in-situ ultrasonic rolling processing on the corrosion resistance of the LDED-UR specimen, a schematic diagram is proposed to describe the corrosion progress in both the LDED and LDED-UR specimens, as shown in Fig. 15.

As shown in Figs. 3 and 15, the surface of the LDED specimen is characterized by unevenness and the presence of multiple pores, resulting in a rough surface. While, the LDED-UR specimen exhibits a comparatively smooth surface with minimal porosity. The surface with high fraction pores facilitates the delivery of electrons, suggesting a rapid



Fig. 15: Schematic diagram of the corrosion processes of LDED (a) and LDED-UR (b) specimens

corrosion rate ^[46]. Additionally, peaks on the surface are more susceptible to corrosion than valleys due to the easier release of electrons ^[47]. Duan et al. ^[48] also stated that pores, act as vulnerable sites, are easily to be attacked by the corrosion solution. For the LDED specimen, a significant contact area between aggressive Cl and the passive film appears, and the peaks on the rough surface are vulnerable to be penetrated by Cl⁻. When the dissolution rate of the passive film exceeds its formation rate, the passive film will be completely penetrated, leading to the formation of a stable corrosion pit. With the continuously progressive of Cl⁻, the corrosion pit becomes deep and wide. In contrast, the contact area between Cl⁻ and the passive film on the flat surface is small for the LDED-UR specimen, making it less susceptible to penetration by Cl. Thus, the corrosion resistance of the LDED-UR specimen with small size and low fraction of pores is superior than that of the LDED specimen.

Based on Figs. 4 and 15, it can be seen that the Cr-enriched ferrite phase is fragmented and homogenized in the LDED-UR specimen. As previously noted, the Cr species is crucial for enhancing the corrosion resistance of stainless steels. For the LDED specimen, a barrier layer is easily formed around the large and inhomogenized ferrite phase. However, this layer is difficult to establish at the location far away from the ferrite phases. Thus, these areas become susceptible to corroded by the corrosive solution, resulting in a reduction in corrosion resistance.

The grain size also plays a crucial role in affecting the corrosion resistance of the studied alloy ^[49]. As illustrated in Figs. 5, 6, and 15, the grains are greatly refined by the application of in-situ ultrasonic rolling, indicating the high grain boundary density. During the electrochemical corrosion process, the grain boundaries can act as nucleation sites for the passive film. Great Cr enrichment caused by the refined grains can be speculated due to high fraction of grain boundaries, which shows positive effects on providing fast diffusion paths for Cr element ^[50]. Along the dense grain boundaries, the fast diffused Cr reacts with oxygen, resulting in the formation of a compact and thick passive film with the high fraction of Cr₂O₃ ^[51]. This compact and thick passive film the high fraction of Cl⁻ passing through the passive film to the alloy ^[52]. Correspondingly,

the rupture of the passive film becomes challenging. Thus, the accelerated formation and adhesion of passive film with high fraction of Cr_2O_3 significantly enhance the corrosion resistance of LDED-UR specimen. In summary, the enhanced corrosion resistance of LDED-UR 316L stainless steel is primarily attributed to the decreased size and fraction of pores, the fragmented and uniformly distributed Cr-enriched ferrite phase, and the development of a compact passive film facilitated by the dense grain boundaries.

5 Conclusions

In this study, ultrasonic rolling assisted LDED hybrid process was developed to enhance the corrosion resistance of the additively manufactured 316L stainless steel. The main conclusions are presented as follows:

(1) The size and fraction of pores can be greatly reduced by applying the in-situ ultrasonic rolling. Austenite and ferrite are the main phases of manufactured 316L stainless steel, and the small size ferrite is homogeneously distributed in the LDED-UR specimen.

(2) For the LDED specimen, the columnar and dendrite grains appear, and their average size is about 63.98 μ m. Fully equaixed grains with an average size of 28.61 μ m are obtained under LDED-UR process.

(3) The corrosion resistance of the LDED-UR specimen is superior than that of the LDED specimen. On the surface of the corroded LDED-UR specimen, small size corrosion pits with low fraction appear. While, they are larger on the surfaces of the LDED specimen.

(4) The enhanced corrosion resistance of the LDED-UR alloy can be ascribed to the small size and low fraction of pores, fragmented and homogenized Cr-enriched ferrite phase, and compact passive film induced by dense grain boundaries.

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Conflict of interest

The authors declare that they have no conflict of interest.

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