The Electropolishing of Additively Manufactured Parts in Titanium: State of the Art

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Recently, additive manufacturing technologies have begun to play a significant role in the industrial field due to the possibility to build complex, near-net-shape, and porous parts, optimizing costs, and time processing. Simultaneously, the high roughness of additively manufactured parts remains a critical drawback, limiting their use like an as-built component. Therefore, postprocessing treatments are needed. The electropolishing (EP) treatment could be ideal for simple, complex, or porous parts characterized by low surface quality. Herein, it is aimed to provide the state of the EP treatment’s art carried out, to date, on additively manufactured parts made of titanium and Ti6Al4V alloy. A scientific literature research on EP of additively manufactured titanium and Ti6Al4V alloy is conducted using the Scopus database. The evaluation of recent research, still very few to date, reveals that a significant reduction of the roughness can also be achieved in complex shape additively manufactured parts. Although the EP is a versatile technique to reduce the roughness of additively manufactured parts, further studies are needed to improve its effectiveness, especially for complex and porous structures, to reduce the environmental impact of the materials used.

1. Introduction

The emerging advanced additive manufacturing (AM) technologies allow the production of 3D metal parts for different applications from aerospace to the biomedical field. The growing interest comes from the possibility to build complex and near-net-shape parts, using relatively short time and in some circumstances at a lower cost of conventional technologies. Several AM technologies have been proposed regarding the powder bed fusion (PBF) processes. The main technologies, which differ for the heat source used (electron or laser beams), are the electron beam melting (EBM) and selective laser melting (SLM) or direct metal laser sintering (DMLS). The SLM process involves the melting of the powders, while the DMLS involves their sintering. The heat source is used to sinter or melt the metallic powder bed. One of the limiting factors of the AM processes is the parts surface quality, which is rough, depending, mainly, on the heat source. The surface quality is strictly related to the building parameters and the complex phenomena occurring during the powders’ melting and solidification or sintering. The rippling, the staircase effects, the balling, and the presence of partially or unmelted particles bonded to the underlying surface are some of these phenomena (Figure 1).[1]

The rippling is the result of the Marangoni effect, activated by a thermal gradient. A temperature difference occurs between the beam and solidifying zone when the focused beam hits the metal powders and moves at high speed. The thermal gradient produces a difference in surface tension between the melted powders under and away from the beam. In turn, the surface tension gradient produces shear forces on the liquid surface, which involves the melted part displacement from the center of the beam toward zones away from it. Generally, this displacement is balanced by a counter flow of melted part toward the beam zone due to gravity forces in a stationary condition. The rapid cooling in the additive technologies freezes this stationary condition, producing a wavy surface.[2,3] The stair-step effect is due to the layer-based nature of the manufacturing process. The layer thickness and the inclination angle adopted during the building process could affect the surface finish.[4] For these reasons, the stair-step effect is especially evident for inclined or curved parts.

On the contrary, the balling phenomenon is the result of the Plateau–Rayleigh capillary instability. At a very high scan speed, the beam melts the powders forming a track of a cylindrical-shaped melt zone. The latter tend to break up into droplets to reduce the surface area and lower its surface energy.[5,6] In particular, the Plateau–Rayleigh instability occurs when the ratio between the length of the molten cylinder pool, L, and the width of the deposit, D, is equal to

$$\frac{L}{D} \geq \pi$$

(1)

The effects just described influence considerably the surface texture of the additively manufactured objects.[7] They involve high roughness values, more pronounced for EBM parts, generally fabricated using larger powders than those used to produce the SLM or DMLS components, as shown in Figure 2. The EBM...
parts can reach a $S_a$ (average roughness) value of about 50 $\mu$m, whereas the DMLS ones can show a $S_a$ value of about 15 $\mu$m.\cite{8}

It is well known that rough surfaces are detrimental to mechanical properties. Irregularities in the surface play a key role in fatigue failure mechanisms, such as crack initiation.\cite{9,10} Also, corrosion phenomena are easily triggered by a rough surface.\cite{11–13}

Two methods could be mainly adopted to improve the surface finishing of AM components. The first one involves an accurate study and use of the process parameters during the manufacturing process, between them: the proper building direction, layer thickness, scan strategy, scanning speed, hatch distance, and go on. Although optimizing the working parameters\cite{14} can reduce the surface irregularities, it is almost impossible, for several applications, to obtain parts that can be used as-built. In contrast, the second method involves postprocessing treatments such as mechanical grinding, chemical, or electrochemical polishing. Several investigations related to the mechanical or chemical polishing post-processing treatment of additively manufactured parts are presented in the scientific literature. Cherry et al.\cite{15} revealed the possibility to reduce the roughness of as-built SLM stainless steel 316L parts by optimizing the hatch distance, the scanning speed, and the exposure time. However, the authors showed that additional postprocessing treatment is generally needed. Zhang et al.\cite{16} investigated the effect of a microblasting treatment on the surface quality of 316L tubular lattice produced by the SLM technique. The effect of shot-peening post-treatment on the fatigue resistance of additively manufactured AlSi10Mg specimens by SLM has been investigated by Uzan et al.\cite{17}. Zhang et al.\cite{18} studied the effect of two-step chemical polishing of as-built additive manufactured Ti6Al4V components. Tyagi et al.\cite{19} studied a chemical polishing method to improve the surface finish of 316 steel additively manufactured components.

As said, mechanical and chemical polishing techniques present several drawbacks. Complex shape parts are difficult, if not impossible, to finish by conventional mechanical treatments. Furthermore, many of them can introduce residual stresses through plastic deformation, altering the original lattice structure. In contrast, chemical polishing requires strong acids, often pollutants, hazardous, and difficult and expensive to dispose of. In addition, it cannot always eliminate sufficiently the surface features of the additive manufactured components.

Electropolishing (EP) could be the ideal candidate for surface treatment of additively manufactured parts. The reasons are related to the possibility of modifying complex shapes and porous...
parts and using environmentally friendly electrolytic solutions. Although the EP is a well-known process used for a long time, researchers have only recently studied its effectiveness on complex additively manufactured parts. Generally, the EP process on conventionally produced parts is carried out on conventionally produced parts to obtain the brightening, i.e., a mirror-like finishing, of the surfaces, usually mechanically ground before the EP process. Whereas the EP treatment on additively produced parts is carried out to obtain a significant reduction of roughness (till few micrometers), i.e., the surface smoothing would say Landol,
keeping the part’s geometry as close as possible to the original. Until now, few papers regarding the EP treatment on additively produced components are present on the Scopus database (see Figure 3). Most of them are addressed to the EP treatment of laser-based manufactured parts and studied simple geometries, often using still hazardous electrolytic solutions. When a complex geometry has been considered, a combination of chemical or mechanical pretreatment and electrochemical polishing treatment was often used to reduce roughness. Roughness measurements mainly evaluate EP’s effectiveness. Often the fatigue performances are investigated, whereas the electrochemical properties of the newly formed surface are rarely studied.

Due to their excellent corrosion resistance and biocompatibility, low density, mechanical properties, titanium and its alloys are widely used in various environments. It is well known that the high corrosion resistance is due to the presence of a chemically stable oxide layer on their surface, making titanium and its alloy suitable for use in several aggressive environments. Ti exists in two different physical crystalline states: body-centered cubic (BCC) and hexagonal closed packing (HCP). Based on the microstructure of titanium alloys, they can be divided into α-type titanium alloys, β-type titanium alloys, and α+β-type titanium alloys. Among the various type of alloy, Ti6Al4V, an α+β-type titanium alloy, is mainly used for many engineering components, from biomedical to aerospace applications. The addition of Al increases the α (HCP) → β (BCC) phase transition temperature from 885 to 995 °C. In contrast, the addition of V, a β phase stabilizing, can create a martensitic structure under deformation. The main hurdles of various potential applications of titanium and its alloys are the cost, and the difficulty to machine them using traditional manufacturing methods, resulting in high manufacturing costs. AM technologies could help in overcoming the limits mentioned earlier. The innovative technologies could represent an energy-effective and time-efficient approach of producing titanium-based parts, allowing their customization. Also, AM technologies could allow designing an object with specific mechanical properties.

This review aims to identify the current state of the art in the EP of titanium and its alloys, focusing on the electrochemical postprocessing treatment reserved for the additive manufactured parts.

2. The EP Treatment

The EP treatment refers to the electrochemical treatment, which removes material from a metallic piece to polish it. A reduction of the large-scale irregularities (smoothing) or the brightening of surfaces is possible to obtain. The former is usually associated with a decrease in roughness in the micrometer range, and the latter achieve specular reflectivity by eliminating irregularities in the sub-micrometer range. Hence, the EP treatment allows obtaining a surface without stresses or deformations compared with the mechanical finishing treatment. The EP treatment involves connecting the material to be polished (the anode) to the positive end of a DC power supply and the cathode to the negative one, as shown in Figure 4. Activation of the current involves an oxidation reaction on the anode and a reduction reaction on the cathode. The process is steered by Faraday’s laws of electrolysis, according to which 1) the amount of material deposited on an electrode due to the flow of current through an electrolyte is directly proportional to the amount of electricity passed through it and 2) the quantity of different substances released by a certain quantity of electricity is proportional to their equivalent chemical weight. As the anodizing, the EP is a process in which many parameters can affect the results, as electrolyte composition, anode–cathode distance, the geometry of anode and cathode, the stirring speed, the temperature, the polishing time, the voltage or current applied, and go on. The electrolytic solutions are often based on hazardous reagents, as perchloric acid or hydrofluoric acid, used in the first experimentations.

Many papers regarding the EP treatment of conventionally produced titanium parts have been published in the past 50 years. All papers aimed to obtain the best polishing of the surface in terms of

![Figure 3](image_url)
3. EP of Additively Manufactured Titanium Parts

If the literature is full of papers that studied the EP process on conventionally produced titanium and its alloys, few investigations still describe the EP process used as postprocessing treatment for additively manufactured parts. Until now, only seven papers on Scopus Database are published. The reason is related to AM technologies, which have very recently aroused a strong industrial interest. As aforementioned, the as-built AM parts are characterized by high roughness values usually ranging from 8 to 50 μm, depending on the AM technology used. Thus, in contrast to the aim of the EP treatment carried out on conventionally produced components, it should be repeated that the EP treatments on these parts aim to reduce the roughness to obtain a smooth surface, not necessarily mirror-like finishing. The review of these studies has been organized based on the AM technology used to build the parts. The first paragraph is related to the laser-based technology, the second paragraph to the electron beam ones, and the last to the effects of treatments combination.

3.1. EP as Unique Postprocessing Treatment: SLMed Parts

Ulea and Brailovski\(^{[32]}\) focused their attention on the influence of initial roughness of SLM Ti6Al4V components containing variably oriented surfaces on the EP effectiveness. In particular, three cathode–anode geometries, fixing the electrodes internal distance at 5 mm, were designed to treat the internal surfaces, hardly accessible by traditional surface finishing technology.

Three different anode geometries have been proposed. An arrangement was designated considering a cylindrical anode for recording the current density versus applied potential curve (cylindrical shape, Figure 5a) and establish the EP potentials range. A V-shaped configuration was designed to study the effect of EP parameters on the roughness, mass loss, and thickness reduction of specimens containing different build orientations (0°, 45°, 90°, and 135°, Figure 5b). Another arrangement was designed to simulate internal surfaces of a tube whose walls constituted by a set of plates printed according to different growing directions (barrel/stave-shaped, 0°, 22.5°, 45°, 67°, 90°, 112.5°, and 135°, Figure 5c). The cathode materials were the same as the anodes, with a V-shaped or barrel configuration fixing their ratio to 2:1. Perchloric acid and glacial acetic acid were used as the electrolytic solution. The EP process was carried out at room temperature, with a magnetic stirring of 100 rpm for 1600 s.

The authors identify the EP range based on prior experiences, in which they found an unstable potential applied for low current density values ($J < 80$ mA cm\(^{-2}\)) and serious pitting for high current density values ($J > 320$ mA cm\(^{-2}\)). Thus, the authors declined to set a minimum and maximum value of total electric charge passed through a unitary surface area of 800 and 5600 mA cm\(^{-2}\) min, respectively. In other words, applying a current density of 160 mA cm\(^{-2}\), the EP treatment can be carried out from 5 to 35 min. The EP treatment was carried out in the current density range of 160–320 mA cm\(^{-2}\), which corresponds to a potential range variable between 14 and 17 V. Albeit, the best results were obtained applying a current density of 240 mA cm\(^{-2}\) (about 15 V) for about 24 min. It is noteworthy that the roughness measurements have been carried out through a profilometer instrument, whose tip radius stylus was 5 μm. After the EP treatment in the best condition, the V-shaped samples still showed remaining waviness but recording the lowest roughness value for the 135° built sample. Regarding the stave shape samples, the EP treatment was carried out for about 27 min at 240 mA cm\(^{-2}\). The initial roughness parameter, $R_a$, varies from about 4–23 μm, passing from 0° to 135° in respect to building direction (see Table 1). The final roughness parameter $R_a$ reached very
low values, of 1.28 and 2.52 μm for 0° and 135°, respectively. In particular, the lowest Rₐ value (0.87 μm), was recorded for a building direction of 112.5°, with a reduction of 92%.

The Rₐ values after EP remained around 0, suggesting a symmetrical height distribution. The final Rₐ values of almost all samples were reduced lower than 3, indicating that the EP process rounds the peaks. Only the sample produced at 90° building direction (generally, the most used building directions) showed a value of Rₐ higher than 3, probably due to the presence of pitting phenomena in the analyzed area.

From the thickness reduction analysis, at thickness reduction was exhibited by the sample manufactured with a building orientation of 135°, which has also recorded the highest roughness parameter. On the contrary, the thickness reduction of the 0° stave is the lowest. The thickness reduction from the 22.5° to 112.5° staves, which have very similar initial roughness values Rₐ, presented a similar trend throughout the EP treatment. The mass loss measurements demonstrated that all the surfaces are reduced linearly with time and that the slopes of all the staves are close, suggesting a uniform polishing. This investigation highlighted the following results: 1) the geometry of anode (V-shaped or stave-shaped) affects the final roughness; 2) increasing duration of treatment, as expected, decrease the roughness; 3) higher initial roughness higher roughness reduction. The interesting results showed combining the thickness reduction and the Rₐ value, which allows defining the EP allowances to reach a specific roughness value and the duration of the process. In other words, the thickness reduction of the material, as expected, decrease the roughness; 3) higher initial roughness higher roughness reduction. The interesting results showed combining the thickness reduction and the Rₐ value, which allows defining the EP allowances to reach a specific roughness value and

| Building direction [°] | 0    | 22.5 | 45   | 67.5 | 90   | 112.5 | 135  |
|------------------------|------|------|------|------|------|-------|------|
| Rₐ initial [μm]        | 3.93 | 12.74| 15.54| 12.25| 11.74| 11.25 | 22.68|
| Rₐ final [μm]          | 1.28 | 3.84 | 1.59 | 1.04 | 1.26 | 0.87  | 2.52 |
| Rₐ initial [μm]        | 0.52 | 0.05 | 0.02 | 0.10 | 0.13 | 0.04  | 0.04 |
| Rₐ final [μm]          | 0.03 | 0.07 | 0.04 | 0.17 | 0.05 | 0.07  | 0.12 |
| Rₐ initial [μm]        | 2.74 | 2.65 | 2.40 | 2.39 | 2.28 | 2.52  | 2.38 |
| Rₐ final [μm]          | 1.94 | 2.10 | 2.35 | 2.16 | 4.65 | 2.04  | 1.87 |

The authors have carried out AFM measurements on the electropolished samples to observe the variation of surface morphology, extending the polishing time from 5 to 15 min. As expected, the texture of the samples was rough or smooth, respectively. Another interesting result of this study was given from the chemical analysis of the oxide film formed at different polishing times. After 5 min of EP treatment, the oxide film covering the polished surface was made of unstable and unprotective titanium oxide, TiO and Ti₂O₃ and aluminum oxide, in the form of Al₂O₃. When the polishing time was extended to 10 min, also the vanadium oxide started to appear but with low intensity. The unstable and unprotective TiO and Ti₂O₃ were replaced by denser and more stable oxides.

The electrolyte composition was composed of perchloric acid and glacial acetic acid. Without recording the classical current density–potential curve, a random current density of 0.3 A cm⁻², a polishing temperature of 30°C, an interspace–electrodes distance of 5 mm, and four polishing times (5, 10, 15, or 20 min) were imposed. The roughness measurements, carried out by a contact profilometer instrument, and weight loss analyses were carried out. The former, shown in Table 2, showed a decrease in the mean roughness value Rₐ from about 7 μm, before the EP, to the lowest value, about 1 μm, with a polishing time of 15 min. The Rₐ value increases again, extending the processing time. In contrast, weight loss continues to increase with the processing time.

Zhang et al. [33] focused their attention on the effect of EP time on the surface composition of Ti6Al4V ELI additively manufactured by the SLM technique tested for biomedical applications. The electrolyte composition was composed of perchloric acid and glacial acetic acid. Without recording the classical current density–potential curve, a random current density of 0.3 A cm⁻², a polishing temperature of 30°C, an interspace–electrodes distance of 5 mm, and four polishing times (5, 10, 15, or 20 min) were imposed. The roughness measurements, carried out by a contact profilometer instrument, and weight loss analyses were carried out. The former, shown in Table 2, showed a decrease in the mean roughness value Rₐ from about 7 μm, before the EP, to the lowest value, about 1 μm, with a polishing time of 15 min. The Rₐ value increases again, extending the processing time. In contrast, weight loss continues to increase with the processing time.

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stable anatase and rutile TiO₂ titanium oxides, and higher peaks of vanadium oxides, in the form of V₂O₃ and V₂O₄, after 15 min of treatment. In addition, the electrochemical behavior has been investigated by potentiodynamic polarization test and electrochemical impedance spectroscopy in a physiological solution used to characterize components for biomedical applications.[21] The EP treatment improved the corrosion resistance prolonging the EP time until 15 min, after which it decreased. The lowest corrosion current was exhibited for a polishing time of 15 min (see Figure 6a), as also confirmed by Body plots, shown in Figure 6b. Also, the impedance modulus increased with extending the EP time until the process is carried out for 15 min.

To model the electrochemical behavior, the authors adopted the Grimm theory, according to which the oxide layer is a bilayer film composed of a compact inner layer and a porous external layer. Thus, they used two equivalent electrical circuits made of one parallel RC circuit or two parallel RC circuits in parallel to fit the electrochemical behavior of the EP process carried out for a time of 5 min or more, respectively. The fitting data confirmed the porous and compact nature of the oxide film when the EP treatment was carried out for times higher than 5 min and revealed the highest value of the resistance of the compact inner layer offered by specimen electropolished for 15 min, suggesting a higher corrosion resistance, as shown in Table 3.

The authors also proposed a controversial electropolished mechanism based on the formation of spherical oxide particles resulting from the reaction of the peaks, which characterized the as-built surface, with the oxygen, probably, present in the electrolyte. During the treatment, the electrolyte acts especially in the necking connecting the oxide particle to the substrate, leading to a peel-off effect of the particles and, in turn, the smoothing of the surface. Therefore, it is not easy to suppose the formation of the oxide only on the peaks of the surface and the formation of spherical oxide particles.

The surface conditions are essential for metallic biomaterials as it controls the cellular attachment and proliferation and affects fatigue performance. Thus, Benedetti et al.[34] explored the morphology features, mechanical properties, and biocompatibility of cylindrical specimens, printed with a building direction of 90°, of SLM Ti6Al4V ELI after different postsintering treatments to identify among them the most appropriate for biomedical applications able to improve the fatigue resistance. Initially, a tribofinishing process was performed on a group of the samples to reduce the initial roughness. After, a shot peening or a hot isostatic pressing (HIP) or an EP treatment was carried out, and the results were compared with each other. In particular, the fatigue tests were carried out exploring fatigue lives between 5 × 10⁴ and 5 × 10⁵ cycles. The EP process was carried out at 70 V for 30 min in an acid-free electrolytic solution, according to Taijima et al.[28] Roughness measurements, carried out by a contact profilometer, showed the roughness parameters shown in Table 4. As expected, the most significant reduction of roughness was obtained through the EP treatment, although the morphological observations revealed a smooth surface characterized by small remnants of unfused particles.

The fatigue curves of the as-built, tribo-finished, electropolished, and HIPed showed a knee around 1 × 10⁶ cycles, as shown in Figure 7. However, the fatigue curves of the shot-peened samples (rhombus dot) steady declined with the fatigue life, showing the highest fatigue resistance in the low-to-medium cycle, equal to 480 MPa.

It can be observed that the ranking of fatigue resistance is as-built < Electropolished < tribo-finished < HIPed. The as-built reached the lowest value, of about 220 MPa at 50 million cycles. The EP treatment improved the fatigue behavior by 14%, recording a value of 250 MPa, probably, due to the exposure of subsurface pores, which act as crack initiation sites. The introduction of surface compressive residual stresses had a more beneficial effect than reducing roughness, as demonstrated by tribofinished samples, which recorded a value of high-cycle fatigue of

Table 3. EIS fitting parameters for Ti6Al4V alloys before and after the EP.

| Polishing time [min] | R_l [Ω cm²] | Q_l [F cm⁻¹] | R_C [Ω cm²] | Q_C [F cm⁻¹] | R_t [Ω cm²] | χ² |
|----------------------|-------------|--------------|-------------|--------------|-------------|-----|
| 5                    | 20.69       | 2.02 E-02    | 758.4       | –            | –           | 2.02 E-03 |
| 10                   | 16.44       | 2.51 E-05    | 8.56        | 2.66 E-06    | 7.15 E + 05 | 1.48 E-03 |
| 15                   | 21.49       | 5.63 E-05    | 12.72       | 3.72 E-06    | 1.01 E + 06 | 7.97 E-04 |
| 20                   | 23.29       | 4.65 E-05    | 23.56       | 2.05 E-06    | 5.13 E + 05 | 1.59 E-03 |

Table 4. Roughness parameters after a different type of postprocessing treatment.

| Condition          | R_h [μm] | R_s [μm] |
|--------------------|----------|----------|
| As-built           | 6.83     | 38.40    |
| Tribo-finished     | 4.96     | 28.10    |
| Electropolished    | 0.54     | 4.41     |
| HIPed              | 5.07     | 35.50    |
| Shot-peened        | 3.36     | 20.05    |

Figure 7. Fatigue curves of the as-built (square dot), tribo-finished (blue triangle dot), electropolished (circle dot), shot-peened (rhombus dot), and HIPed (purple triangle dot) samples. Reproduced with permission.[34] Copyright 2020, Elsevier.
340 MPa. The highest fatigue endurance equal to 370 MPa was exhibited by the HIPed sample due to the reduction of the porosity over the entire thickness and of the sintering-induced defects through the fusion of unmolten particles, in addition to the introduction of a compressive residual stresses condition. In terms of cell growth at different times, the biological properties were investigated only on the two surface treatments that most changed the surface topography as the EP, which reduces the roughness, and the shot peening that introduces a pattern of dimples. Both treatments showed quite similar behavior regarding cell growth and proliferation. Thus, the selection of the best post-sintering treatment is driven by other consideration, as the high fatigue resistance or the process cost and duration.

3.2. EP as Unique Postprocessing Treatment: EBMed Parts

It is well known that the EBM parts show a higher roughness surface compared with that exhibited by laser-based additively manufactured specimens. Wu et al.\textsuperscript{[35]} studied the effect of the EP on biocorrosion and mechanical properties of Ti6Al4V tensile test specimens (Figure 8), printing with a building direction of 90° by EBM technology.

The lateral surface, which is generally mainly affected by the parameters of the contour melting, was chosen to characterize the relationship between surface roughness and tensile/biocorrosion behavior. The EP treatment was carried out using a mixed electrolytic solution of perchloric acid, acetic acid, and ethanol, at 4 °C and magnetically stirring at a rate of 800 rpm. Surface morphology and chemical composition analysis, mechanical characterization, biocorrosion behavior analyses were carried out. Although the current density–potential curve has been recorded, also, in this case, no limiting current plateau, as reported by Urlea and Brailovski.\textsuperscript{[32]} The authors carried out the EP treatment in a possible EP zone (marked with red lines in Figure 9), defining three specific values of current density equal to 147, 294, or 442 mA cm\textsuperscript{-2}.

Furthermore, they carried out the EP treatment, fixing a value of potential (equal to 15 V) in the same range aforementioned for 20 min. Starting from an initial roughness value \( R_s \) of the lateral surface of 24 μm for the unpolished specimen, the authors reported a final roughness value of about 15, 10, and 5 μm for the increasing currents density values aforementioned. A higher current density value involved a greater reduction of the roughness. The chemical analysis revealed that after the EP process on the surface, in addition to Al\textsubscript{2}O\textsubscript{3} and V\textsubscript{2}O\textsubscript{5} oxides, there was a more homogeneous TiO\textsubscript{2} layer than the unpolished specimen. The mechanical characterizations, investigated by tensile tests, demonstrated that the elastic modulus and yield stress were not affected by the EP treatment and the surface roughness, as shown in Table 5. In contrast, a gradual improvement of the ultimate tensile stress and tensile elongation was exhibited.

The biocorrosion analysis was carried out by open-circuit potential (OCP) and potentiodynamic polarization analysis. The OCP value, shown in Figure 10a, decreases by reducing the roughness, from 24 to 15 μm. On the contrary, a further reduction of roughness involved an increase in the OCP value. The reduction of the roughness involves an increase in the corrosion potential, \( E_{corr} \), and a decrease in the corrosion current density, down to 15.47 nA cm\textsuperscript{-2} for the specimen with a roughness value of 10 μm (green curve), as shown in Figure 10b. A lower value of roughness, on the contrary, showed a higher corrosion current density due to an overpolishing treatment that involved the formation of some tiny black dots on the surface. A broad passivity was observed for all electropolished samples, although a light instability over 1.5 V versus Ag/Cl was exhibited, as reported in the literature.\textsuperscript{[8]} In conclusion, the lowest roughness (4.5 μm) did not seem to have any detrimental effect on the mechanical performance; in contrast, the biocorrosion resistance slightly degraded. Thus, the authors suggested carrying out the EP in proper condition, avoiding reducing overly the roughness.

![Figure 8](image-url) Ti6Al4V EBM-produced tensile test specimen.

![Figure 9](image-url) Current density versus potential curve of Ti6Al4V EBM manufactured parts. Reproduced under terms of the CC-BY license.\textsuperscript{[35]} Yao-Cheng Wu, Che-Nan Kuo, Yueh-Chun Chung, Chee-How Ng, and Jacob C. Huang, published by Materials.

| Condition         | Young modulus [GPa] | Yield stress [MPa] | Ultimate tensile stress [MPa] | Tensile elongation [%] |
|-------------------|---------------------|--------------------|-------------------------------|------------------------|
| Unpolished \((R_s = 24 \mu m)\) | 100 ± 2             | ≈                  | 995 ± 8                       | 7.6 ± 0.4              |
| Polished 1 \((R_s = 15 \mu m)\) | 103 ± 2             | 817 ± 2            | 1012 ± 13                     | 8.7 ± 0.5              |
| Polished 2 \((R_s = 10 \mu m)\) | 100 ± 1             | 809 ± 5            | 1025 ± 7                      | 9.3 ± 0.4              |
| Polished 3 \((R_s = 4.5 \mu m)\) | 102 ± 3             | 817 ± 2            | 1052 ± 8                      | 11.6 ± 0.7             |

Table 5. Results of the tensile test carried out on Ti6Al4V EBM produced.
The surface complexity of additively fabricated parts has encouraged some authors to investigate the effect of a combination of chemical etching followed by electrochemical polishing. Longhitano et al.\[36\] studied the surface finishing of cylindrical DMLS Ti6Al4V alloy parts exposed to blasting or chemical etching or EP treatments as a single or combined process. Roughness (Ra, Rz), mass loss measurements and morphological observations were carried out. The electrochemical polishing was carried out in the most used and hazardous solution, made of perchloric acid and acetic acid, applying a random potential of 55 V for 5 min at room temperature (Table 6).

The lowest roughness parameter, Ra, was recorded for the combination of blasting treatment and chemical etching, carried out in a nitric–hydrofluoric acids solution. Considering every single treatment, the surprising result, in comparison with the other studies here reported, is the highest final roughness value recorded for the only EP treatment. The initial roughness value of about 6 μm was increased to about 7.5 μm, although the sample presented a mirrored surface finish. The mass analysis shows a reduction in weight for all treatments. Among the single treatments, the highest mass reduction was shown by the only etching treatment, probably due to the complete immersion of the sample in the acid bath, as claimed by the authors. The authors asserted that the combination of the blasting and the chemical etching is effective to reduce the roughness of DMLS AM parts.

Dong et al.\[37\] proposed an interesting although garbled and twisted investigation. The authors applied a Taguchi DOE approach to study the effectiveness of roughness improvement of a treatment’s combination, chemical etching, and EP, carried out on DMLS Ti6Al4V lattice structures, whose picture is shown in Figure 11a. The complex components were manufactured so that the top and back surfaces faced the build platform, removed by milling after the fabrication. Therefore, the top and back were not included in the investigation. The three holes have been drilled after the building process as identification marks to compare the as-built and post-processed samples.

Two sets of surfaces have been considered: external (Figure 11a: right, front, bottom, and left) and internal (Figure 11b: Section 1, Section 2 front, Section2 back, Section 3, flat 1, flat 2, and flat 3). In addition, the supported surfaces were differentiated from unsupported surfaces, as shown in Table 7.

The chemical etching involved the use of the nitric–hydrofluoric acid bath, as often reported in the literature for conventionally produced titanium and its alloys. An ethanol-based electrolytic solution similar to the study by Tajima et al.\[28\] has been used for the EP treatment.

The authors applied the Taguchi approach to study the parameters with the most influence on the roughness. As a matter the fact, it is well known that the Taguchi method allow conducting a minimal number of experiments which could give the full information of all the factors that affect the process performance in the exam. Thus, a Z\(^2\) factorial design was used choosing the following parameters: 1) the voltage, 2) the time of the EP, and 3) the etching time. For each parameter, two values were chosen as a result of preliminary testing. In particular, the voltage could assume a value of 40 or 50 V; the EP was carried out for 10 or

### Table 6. Roughness parameters and mass values of DMLS Ti6Al4V processes with different treatments.

| Condition                           | Ra [μm] | Rz [μm] | Mass [g] | Reduction [%] |
|-------------------------------------|---------|---------|----------|---------------|
| As-built                            | ≈6.1    | ≈29     | 1.71     | –             |
| Chemical etched                     | ≈6.2    | ≈35     | 1.59     | 7.03          |
| Electropolished                     | ≈7.5    | ≈47     | 1.68     | 1.58          |
| Blasted                             | ≈5.0    | ≈27     | 1.69     | 1.17          |
| Blasted and chemical etched         | ≈4.2    | ≈20     | 1.59     | 6.97          |
| Blasted and chemical etched and electropolished | ≈6.8    | ≈51     | 1.56     | 8.96          |
15 min, and the etching time for 0 or 15 min. In summary, eight experiments were analyzed in replicating the experiment two-fold, as shown in Table 8.

At first, the roughness measurements were carried out on each surface of 12 as-built samples, selecting eight of them with the minimum standard deviation. Two other samples have been selected to validate the process and consider the impact of the initial roughness. They are shown as Val 1 and Val 2 in Table 8.

The roughness results are shown in Figure 12. As can see, the internal surfaces (Figure 12b) exhibited higher roughness values compared with the external ones (Figure 12a). In particular, the unsupported internal surfaces present higher roughness values than the supported internal ones due to the lack of supports. Then, the authors carried out the experiments following the combination given by the DOE.

The etching treatment certainly reduced the average roughness on the internal and external surfaces compared with the as-built sample, as shown in Figure 13, but with a substantial difference. The etching treatment on the external and internal supported surfaces involved a similar reduction of the roughness parameter, between 5 and 7 μm, although an uneven initial roughness. In contrast, the chemical treatment on the unsupported internal surfaces with a higher initial roughness involved greater values than the supported surfaces, highlighting the influence of the original roughness. However, the etching treatment allows reducing the standard deviation between the different sets of surfaces. The SEM micrographs carried out after the etching treatment allowed observing a uniform finishing except in the corners still covered by partially melted particles, probably due to the short treatment time, and in turn, to the poor flow conditions. At the same time, pitting phenomena have been detected because of the composition of the alloy, made of alpha and beta phases which react at a different rate to the chemical reagents. The analysis of the DOE revealed that the higher etching treatment involved greater percentual improvement of the roughness reduction and that the higher polishing time and voltage also increased the results’ value. Thus, the combination of 15 min of etching, 15 min of EP and 50 V of tension was adopted as the optimal condition and validated with two further experiments.

The EP treatment was not uniform between the surfaces (see Figure 13). In particular, the following considerations were drawn. The “flat” surfaces were not modified by the EP process, compared with the external ones, which recorded a considerable polishing. Due to the proximity to the cathode, the “front” surface presented the lowest roughness value. Although the “bottom” surface exhibited the minor reduction due to an “edge effect,” i.e., a faster metals dissolution of the sharp edges, as confirmed by MicroComputed Tomography dimensional (MCT) analysis. The authors have demonstrated that the edge effect can be decreased by etching treatment before the EP.

Table 7. Identification of the different considered surfaces.

| SET SURFACES |  |  |  |  |  |
|--------------|---|---|---|---|---|
| External supported | Right | Front | Bottom | Left |
| Internal supported | Section2 front | Section 3 | Flat 3 | Flat 1 |
| Internal unsupported | Section2 back | Section 1 | Flat 2 | – |

Table 8. DOE using the Taguchi approach.

| Experiment | Etching time [min] | EP time [min] | Voltage [V] | Experiments codes |
|------------|---------------------|---------------|------------|-----------------|
| 1          | 0                   | 10            | 40         | S11             |
| 2          | 0                   | 15            | 50         | S21             |
| 3          | 15                  | 10            | 50         | S31             |
| 4          | 15                  | 15            | 40         | S41             |
| 5          | 0                   | 10            | 40         | S12             |
| 6          | 0                   | 15            | 50         | S22             |
| 7          | 15                  | 10            | 50         | S32             |
| 8          | 15                  | 15            | 40         | S42             |
| –          | 15                  | 15            | 50         | Val 1           |
| –          | 15                  | 15            | 50         | Val 2           |
An interesting analysis was carried out by a microcomputed tomography dimensional characterization. The results data have shown that the etching treatment has an isotropic tendency. A uniform material loss after etching treatment (Figure 14a) was observed except on the corners of diagonal strokes, probably due to the pronounced stair-step effect during the printing process.

Also, the electrochemical polishing was more effective on the external features than the internal one, probably due to the low conductivity of the electrolyte. In addition, the surfaces closer to the cathodes have exhibited a more evident roughness decrease, as well as the edges showed the lowest roughness value due to a more pronounced dissolution. An evident material loss was observed on the edges after the EP process (Figure 14b). In conclusion, the authors claimed that a combination of etching and EP treatment helps to reduce roughness. The etching treatment produced a uniform attack, reducing the internal and external surfaces. On the contrary, EP is more effective on the external features than the internal ones. The authors suggest addressing the future works on the optimization of the chemical composition of the electrolyte to reduce the edges’ effect and the removal of materials.

Pyka et al. [38] modified cylindrical porous structure of SLM-produced Ti6Al4V parts (a particular is shown in Figure 15) using chemical etching and electrochemical polishing treatments both carried out using electrolytic solutions based on hydrofluoric acid.

In particular, the electrolyte solution used for EP was composed of hydrofluoric acid, acetic acid, and sulfuric acid. The treatments investigated, shown in Table 9, were: the only etching, the only EP
treatment carried out for 2, 4, 6, or 8 min, the etching treatment carried out before the EP performed for 6 or 8 min, for a total of seven combinations. Also in this case, a random current density of 1.2 mA mm$^{-2}$ was applied. The authors investigated the influence of the etching and polishing time on final surface roughness.

The cylindrical geometry of the parts did not allow the use of classic roughness measuring instruments; therefore, the roughness characterization was carried out by processing with an internally developed MATLAB tool the digital images of the embedded samples before and after the postprocessing treatments. In addition, morphological observations and mechanical analysis were carried out. The initial and significantly inhomogeneous roughness between the values recorded on the top and the bottom decreased with increasing polishing time, as shown in Figure 16a. The chemical etching and the EP treatment carried out for a long time, carried out individually, have reduced the roughness value of the bottom surface more than the top one. In contrast, the efficiency of the EP treatment required too long times, resulting in a significant decrease in the thickness beyond the roughness. Therefore, the authors claimed that the combination of chemical etching and EP for 8 min seems to be the most effective in obtaining a sufficiently uniform and controlled roughness.

Microcomputed tomography analysis was also carried out to evaluate the influence of the surface modifications on the global porous structure morphology. The only chemical etching and the combination of chemical etching and EP (8 min), although showed the lowest roughness, exhibited on the other hand a significant volume reduction, which unavoidably affected the mechanical performance, whose results are shown in Figure 17.

In summary, this review emerged that EP treatment parameters are often chosen without a clear modus operandi rather than on preliminary experiments or by adopting treatment procedures performed on conventionally manufactured components. Although eco-compatibility issues are at the heart of the international scientific and political debate, dangerous acid-based electrolyte solutions are still used. The initial roughness plays a fundamental role. The greater the initial roughness, the greater the reduction obtained with an EP treatment. Nevertheless, the initial roughness is linked to the building phase of the component, on which it may not be easy to modify, it is possible to adapt and control appropriate values of the parameters that influence an EP treatment such as the duration, the driving force values, the chemical composition of the electrolytic solution. An EP treatment carried out for a long time (greater than 15–20 min) or applying a high current density value reduces the roughness but at the same time reduces the thickness and the volume. A less-conductive electrolytic solution would limit the edge effect found in sharp-edged parts. It goes without saying that to adopt

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Table 9. Conditions and nomenclature of the treatments carried out on porous cylindrical structure of SLM-produced Ti6Al4V parts.

| Condition      | Nomenclature |
|----------------|--------------|
| As-produced a-p |              |
| Etching        | CHE          |
| EP for 2 min   | ECP-2        |
| EP for 4 min   | ECP-4        |
| EP for 6 min   | ECP-6        |
| EP for 8 min   | ECP-8        |
| Etching + EP for 6 min | CHE-ECP-6 |
| Etching + EP for 8 min | CHE-ECP-8 |

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Figure 14. Simulation by MATLAB of mass loss after a) etching or b) EP treatments (the red color represents the region with the most significant material loss). Reproduced with permission,[37] Copyright 2021, Springer, Nature.

Figure 15. SEM picture of a) the unit cell and b) a particular of a strut surface where the unmelted powder particles could be present on top (T) and bottom (B). Adapted with permission,[38] Copyright 2020, John Wiley and Sons.
EP as a postprocessing treatment, it is necessary to find the optimal point between the reduction of roughness and the loss of thickness or mass. Considering the complex and porous structures, in which the problems are amplified due to the difficulty of effectively and uniformly carrying out the treatment, especially on the internal surfaces, which are less accessible, further and in-depth studies are needed to investigate not only the process feasibility but also the subsequent characterization, which is currently very complex.

As for the physical performance that this process allows obtaining, the following conclusions can be drawn. EP treatment certainly improves resistance to biocorrosion, excluding the AM technologies adopted, as reported by Zhang and Wu, due to the formation of mixed oxides that form and coat the surface during the treatment. Both studies presented here provide interesting information regarding which parameters to modify to improve the electrochemical response. Zhang et al. suggest carrying out the EP treatment for a maximum duration of 15 min because prolonged processing times increase the surface roughness and, at the same time, decrease the corrosion performance. Wu et al. is recommended applying a specific current density value to avoid a superpolishing effect of the surface with pitting phenomena.

### Table 10. Summary of the electropolished conditions adopted and roughness values results obtained by all the papers reviewed regarding the EP performances on titanium and Ti6Al4V alloy additively manufactured parts.

| Year   | References | AM process | Electrolyte                                                                 | Current or voltage Time/Temperature | Ra initial [μm] | Ra final [μm] |
|--------|------------|------------|------------------------------------------------------------------------------|-------------------------------------|----------------|---------------|
| 2017   | Urlea[32]  | SLM        | Perchloric acid, glacial acetic acid                                         | 240 mA cm⁻² 1600/23°C              | Complex        | Complex       |
| 2018   | Zhang[33]  | SLM        | Perchloric acid, glacial acetic acid                                         | 300 mA cm⁻² 0–1200/30°C 7/1        |                 | 0.54          |
| 2017   | Benedetti[34] | SLM        | Ethyl alcohol, isopropyl alcohol, zinc chloride, aluminum chloride          | 70 V 1800/30°C 6.83                  |                 | 0.34          |
| 2019   | Wu[35]     | EBM        | Perchloric acid, acetic acid and ethyl alcohol                              | 147.294.442 mA cm⁻² 1200/– 24.15.10.5 |                 |               |
| 2015   | Longhitano[36] | DMLS      | Perchloric acid, acetic acid and ethyl alcohol                              | 55 V 300/23°C 6/8                   |                 |               |
| 2019   | Dong[37]   | DMLS       | Ethyl alcohol, butyl alcohol, zinc chloride, aluminum chloride             | 40–50 V 600–900/– Complex Complex   |                 |               |
| 2012   | Pyka[38]   | SLM        | Hydrofluoric acid, acetic acid and sulphuric acid                           | 1.2 mA mm⁻² 120–480/– Complex Complex|                 |               |
Regarding the mechanical properties, the resistance to fatigue, traction and compression were studied. All authors agree with a significant improvement in mechanical properties after an EP treatment, carried out alone or combined with a previous etching chemical treatment.

The EP conditions adopted and the roughness measurement results in the investigations related to the EP postprocessing treatment applied on titanium additively manufactured components, aforementioned, are shown in Table 10.

4. Conclusions

The growing interest in AM technologies comes from the possibility of building complex and near-net-shape parts quickly, avoiding the long processes of conventional technologies. A limiting factor of the additive technologies is the as-built surface quality, characterized by high roughness values, which involves necessary post-processing treatments. This review aimed to identify the current state of the art in the EP process on titanium and its alloys, focusing the attention reserved to the additively manufactured parts. The application of the EP process on additively produced parts presents a very ambitious challenge, which must take into account the very complex nature of the surface morphology that characterizes the new components. To significantly reduce the roughness of the surfaces without necessarily polishing them is the main objective. From the review, it emerges that the EP post-processing treatment: 1) allows a significant reduction of roughness complex shape parts, but it is more effective on the external features compared with the internal one, probably due to the low conductivity of the solution; 2) it can improve the fatigue behavior as well as the corrosion resistance. The consequent loss of mass after the EP treatment is possible to quantify to both remain within the design tolerances and ensure desired mechanical properties.

In contrast, well-known and classic and hazardous electrolytic solutions are still used for complex shape parts. There are many challenges the scientific community will still have to face to improve the extraordinary advantages of the EP treatment and also to adopt low environmental impact solutions.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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