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Review paper

Electrochemical surface modification of Ti6Al4V: positioning electrochemical machining as a low-valence dissolution pathway for enhanced performance

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Abstract

The automotive, aerospace, biomedical, and other engineering sectors make substantial use of Ti6Al4V titanium alloy, known for its high strength-to-weight ratio, corrosion resistance, and biocompatibility, but it often suffers from poor tribological performance and low surface hardness. To increase durability, a variety of surface modification techniques have been investigated, including chemical etching, shot peening, thermal oxidation, laser surface texturing, and physical vapor deposition. However, these methods frequently entail high thermal input and mechanical stress with limited control over surface chemistry. Electrochemical methods, on the other hand, allow uniform and precise alteration of surface morphology without thermal or mechanical damage. Among these, anodization and plasma electrolytic oxidation (PEO) facilitate hardening and stress-free surfaces but suffer from passive film formation, porosity and micro-cracks, while electrochemical polishing (ECP) yields much better surface finish but at high energy cost and causes passive film formation. In this review, electrochemical machining (ECM), typically viewed as a subtractive method for material removal, is reevaluated as a process for both material removal and functional surface tailoring. Despite its application for removing material, ECM promotes valence-controlled dissolution that favours the formation of lower oxidation states of titanium. It also inhibits the formation of passive films and enables the formation of atomically smooth surfaces. The present study provides a novel theoretical framework for customizing Ti6Al4V surfaces with improved functional and morphological properties by integrating ECM with anodization, PEO and ECP within the broader paradigm of electrochemical surface engineering.

Keywords

Titanium alloy; surface modification techniques; anodization; plasma electrolytic oxidation; electrochemical polishing; valence-controlled dissolution

Introduction

Because of favourable characteristics, titanium and its alloys, especially Ti6Al4V, have established a cornerstone position among advanced engineering materials that are desirable for applications requiring high performance in a variety of industries, including maritime engineering, biomedical implants, and aerospace [1]. However, despite its impressive bulk properties, Ti6Al4V is found to have several surface-related issues that limit its ideal use in practical applications. These include low hardness, poor tribological performance, and increased vulnerability to galling or adhesive wear, particularly in dry or high-friction environments [2,3]. The self-generating nature of a passive titanium dioxide (TiO_2) layer is a major contributor to these limits. Although it improves corrosion resistance, it also increases surface brittleness and reduces wear resistance [4]. Moreover, post-processing surface modification is necessary to improve component life and function due to the alloy's low thermal conductivity and ongoing chemical reactivity during machining, which leads to rapid tool wear and compromised surface integrity [5,6]. Thus, applications in high-performance sectors require more and more surfaces to achieve optimal performance by combining corrosion resistance and mechanical durability under destructive and repeatable conditions. Creating these multifunctional surfaces is critical for aerospace and marine equipment, which generally operate under extreme conditions and high stress, as well as for biomedical implants, which are biocompatible and biointegrated [7,8]. Attempts to control surface chemistry, induce microstructural heterogeneity, and introduce residual stresses through thermal and chemical surface treatments such as chemical etching, thermal oxidation, and shot peening have largely gone unaddressed. As a result, existing techniques fail to produce stable and precisely engineered surfaces required for next-generation applications [9,10].

To address these issues, various surface modification techniques, ranging from mechanical, chemical, thermal, and physical methods to electrochemical procedures, have been investigated. Physical processes such as physical vapor deposition (PVD) and laser surface texturing are commonly used to deposit wear-resistant films or form microtextures to improve surface function [11-14]. However, these methods involve high processing temperatures and lead to increased residual stresses or microstructural inhomogeneity due to their dependence on vacuum requirements and the challenges associated with advanced machinery. Similarly, mechanical techniques such as abrasion blasting and shot peening have been used to increase fatigue strength; they do not address surface chemistry [15]. Although chemical treatments such as acid etching and alkaline activation result in irregular surface features, controlling morphology in these methods is simpler and less precise [16]. Unlike these methods, a variety of electrochemical techniques can be used to alter the surface characteristics of Ti6Al4V, ranging from the formation of modified oxide layers to induced dissolution [17]. Of these techniques, plasma electrolytic oxidation (PEO) and anodizing are widely used to increase bioactivity, corrosion resistance, and hardness [18,19]. The PEO technique, however, results in thick, porous, microcracked ceramic coatings, which affect their structural homogeneity due to the plasma discharge, whereas anodizing creates thin oxide films with low wear resistance [20,21]. Thus far, electrochemical polishing (ECP) is another competitive electrochemical technique that achieves enhanced surface smoothness, particularly at high current densities. This technique primarily improves surface finish through controlled anodic dissolution, resulting in a smooth, brilliant surface. Though it is very effective in removing surface irregularities, it gives limited control over deeper surface chemistry [22]. In addition, since ECP relies on harmful electrolytes and consumes significant energy, questions arise about its environmental friendliness and suitability for specific applications [23]. Electrochemical machining (ECM), on the other hand, is traditionally known as a method for precise material removal. In recent years, it has also been applied as a surface treatment method, enabling controlled ionic dissolution of metals and their alloys through proper tuning of process parameters [24,25]. Such an arrangement favours low-valence titanium species, Ti^+ and Ti^{2+}, which thermodynamically mitigate salt precipitation while simultaneously preventing passivation, and thus, enabling a homogeneous, oxide-free surface. Therefore, ECM has been identified not only as a machining process but also as an electrochemical, complementary surface engineering method similar to anodization, PEO, and ECP [26,27]. This review provides a deeper understanding of how manipulating key parameters, such as applied potential, current density, and electrolyte composition, enables controlled dissolution pathways to access tailored surface properties [28].

This work does not attempt an exhaustive survey but rather demonstrates that low-valence electrochemical dissolution, when properly controlled, can produce surface finishes comparable to or better than those from electrochemical polishing, with added advantages such as reduced power consumption, stress-free surfaces, and improved functional cleanliness. With this emphasis, the present review, within reasonable limits, addresses the electrochemical surface modification of Ti6Al4V, with a focus on ECM as a valence-controlled dissolution process. It undertakes an analysis and evaluation of the available literature. The pathways of surface dissolution and the resulting finishes, in this context, are defined by the applied potential, current density, and electrolyte composition, including additives and nanoparticles, which must be introduced to maintain an appropriate balance of pH and concentration. By placing ECM within a broader integrated electrochemical approach that includes anodization, PEO, and ECP, this work highlights its novelty as a complementary approach to address ongoing challenges with passivation, surface irregularities, and limited tunability. The review thus provides new insights into how electrochemical pathways can be designed to synergistically engineer Ti6Al4V surfaces with enhanced functionality and stability, spanning advanced biomedical to aerospace and high-performance engineering applications.

Classical electrochemical surface modification approaches

Anodization

Anodization is a well-known electrochemical surface treatment technique that modifies surface properties by controlled anodic oxidation of titanium and its alloys, such as Ti6Al4V [29]. To achieve this, an anodic voltage is applied to the immersed titanium substrate in an electrolyte, resulting in the formation of a dense passive TiO_2 film. Such a film enhances resistance to corrosion and biocompatibility and provides tuneable morphology, such as thickness, porosity, and even surface coloration, based on the voltage and composition of the electrolyte used in its processing [30,31]. In biomedical applications, anodized Ti6Al4V surfaces enhance osseointegration by inducing nanoscale changes in surface roughness and chemistry, thereby improving cell attachment and bone bonding. In aerospace and chemical environments, the oxide layer acts to offer protection against oxidation, pitting, and aggressive corrosion [32].

In general, the oxide coatings formed are thin, a few micrometres and can lack sufficient mechanical strength or wear resistance. Under thermal or mechanical stress, these layers may easily crack or delaminate [33]. Moreover, the presence of oxides may restrict subsequent surface functionalization or passivation in more sophisticated surface treatments. Anodization, while low-cost, environmentally benign, and scalable, may often need to be combined with complementary methods, such as PEO or ECM, to achieve enhanced surface durability and functionality under severe service conditions [34].

Plasma electrolytic oxidation

Plasma electrolytic oxidation, also known as microarc oxidation (MAO), is an advanced electrochemical surface treatment used to create thick, hard, ceramic-like oxide coatings on valve metals such as titanium, aluminium, and magnesium alloys [35]. For Ti6Al4V, PEO is carried out at high voltages (typically 200-600 V) in aqueous electrolyte, resulting in localized microarc discharges that transform the metal surface into a crystalline TiO_2-based oxide [36]. This layer is generally porous and adheres well to the substrate, thereby considerably improving wear resistance, corrosion protection, and thermal stability. PEO-treated Ti6Al4V has thus found numerous applications in aerospace, marine, and biomedical applications [37]. In biomedical applications, the porous surface provides opportunities for attaching bone cells and can be designed with bioactive additives such as calcium, phosphorus, or silver, which enhance bone growth or prevent bacterial growth [38]. However, the process faces several challenges, including high energy consumption, induced thermal stresses, coating porosity and appearance of microcracks, which in most cases need sealing post-treatment [39].

In addition, controlling the oxide morphology, porosity, and phase composition remains difficult due to the instability of plasma discharges [40]. Notwithstanding these limitations, PEO remains a feasible approach for developing strong surfaces on Ti6Al4V, especially when optimized via electrolyte engineering or hybrid processing to enhance coating performance and reproducibility [41].

Electrochemical polishing

Electrochemical polishing is a highly advanced surface-finishing process that produces ultra-smooth, clean, oxide-refined surfaces through controlled anodic dissolution. In this process, the Ti6Al4V workpiece serves as anode and is immersed in an acidic electrolyte, commonly a perchloric acid mixture and a cathode completes the electrical circuit [42]. By optimizing current density and voltage, microscopic surface peaks dissolve selectively, leaving a very smooth, mirror-like surface. ECP is especially valued in uses where a surface roughness of < 0.1 µm is of critical concern, *e.g.* biomedical devices, aerospace components, and vacuum or clean room applications [43]. For Ti6Al4V, ECP improves biocompatibility, reduces bacterial adhesion, and enhances corrosion resistance by removing microdefects and exposing a flat oxide layer [44]. This process also eliminates embedded contaminants, improving surface cleanliness and fatigue life. However, the process demands close control of electrolyte chemistry, temperature and current parameters and utilizes hazardous chemicals. Unless properly controlled, over-polishing, pitting, or uneven dissolution can take place [45]. Moreover, rapid passivation in air tends to limit the dissolution efficiency of Ti6Al4V. ECP does not significantly alter mechanical and tribological characteristics; therefore, it is usually used as a final finishing technique, in combination with other techniques to achieve integrated surface engineering [46,47].

Transition to electrochemical machining as a non-traditional electrochemical approach

Compared with oxidation-based electrochemical methods such as anodization or PEO, ECM primarily operates through controlled anodic dissolution of the workpiece. Even though ECM is still seen as a precision-machining method, recent studies have shown that it can also be considered a surface modification method, provided dissolution is controlled via low-valence pathways. This perspective views ECM as a complementary, rather than a different, electrochemical approach. ECM is a stress-free method that does not require mechanical contact and can dissolve anodic material embedded in the electrolyte via electrochemical processes [48]. For alloys such as Ti6Al4V, this expands the utility of ECM for surface precision engineering rather than merely traditional precision machining. Under optimized potentials and electrolyte conditions, ECM enables the oxidation of titanium to its low-valence states (Ti^+, Ti^{2+}, Ti^{3+}), thereby inhibiting the formation of passivating TiO_2 and ensuring uniform, oxide-free dissolution [49]. This process enhances surface homogeneity and morphological uniformity while suppressing micro-precipitation, which is critical for biomedical and aerospace applications [50].

Unlike ECP, which primarily smoothes the surface and has limited control over ionic valence, ECM allows greater control through variables such as applied potential, current density, and additives like reducing agents, complexing agents and nanoparticles. These variables affect the dissolution pathways, and consequently, the type of oxides formed, passivation, and surface roughness [51]. While ECM is, in principle, an adjustment of process parameters such as inter-electrode gap, electrolyte flow, and current density, its thermodynamic adaptability implies that the process can also be a platform for advanced surface modification and refinement [52]. More recent works characterize ECM in surface engineering as thermodynamically efficient, with certain steps beyond mere subtractive processes [53,54]. In the context of titanium and its alloys, multiple oxidation states, Ti^{4+}, Ti^{3+}, Ti^{2+}, and Ti^{+} are exhibited during electrochemical dissolution; however, Ti^{4+} is the dominating ionic species, promoting passive film formation, pitting, and surface roughening [55]. However, operation in the active potential region makes Ti^{3+} dominant, and even more advantageously, valence states below Ti^{3+} give rise to smoother, oxide-free surfaces [56,57]. Although traditionally considered separate from anodization, PEO, and ECP, ECM enables valence-controlled surface chemistry and morphology, positioning it as a versatile electrochemical surface engineering approach for tailoring the functional performance of Ti6Al4V.

Comparative evaluation of electrochemical surface modification techniques for Ti6Al4V

The key performance attributes, such as surface roughness, oxide porosity, structural uniformity, and energy efficiency, are compared for commonly used electrochemical surface treatments of Ti6Al4V in Table 1. This comparison shows the sharp divide between film-based approaches and dissolution-controlled ECM. This assessment emphasizes the relative merits of ECM for attaining uniform, smooth, and oxide-free surfaces under optimized conditions.

Table 1. *Comparative assessment of electrochemical surface modification techniques based on surface attributes for Ti6Al4V alloy*

Surface attribute	Anodization	PEO	ECP	ECM
Surface roughness	High roughness	High roughness	High roughness	Smooth surface finish
Oxide porosity	High porosity	High porosity	High porosity	Low porosity
Uniformity	Non-uniform layers	Non-uniform surface structure	Non-uniform surface structure	Highly uniform treatment
Energy efficiency	Low efficiency	High energy consumption	High energy consumption	High energy efficiency

Table 2 summarizes major electrochemical treatments for Ti6Al4V, highlighting typical surface features, efficiencies, limitations, and associated trade-offs.

Table 2. *Comparison of the different electrochemical surface treatment techniques for Ti6Al4V*

Technique	Effectiveness	Limitations	Surface results/features	Ref.
Anodization	1. Enhances corrosion resistance and biocompatibility 2. Forms an oxide layer with tuneable thickness	1. Thin coatings with low wear resistance 2. Prone to cracking under stress	1.TiO_2 layer 2. Porous or barrier-type surface 3. Improved cell adhesion	[58-60]
PEO	1. Forms thick, hard, ceramic-like coatings 2. Good for wear and corrosion resistance	1. Require high voltage 2. Coatings can be porous and cracked 3. Poor control of micro-structure	1. Crystalline TiO_2 with dopants 2. Porous and rough texture 3. High hardness (400 to 800 HV)	[61,62]
ECP	1. Excellent surface smoothness 2. Reduces micro defects and embedded particles	1. Limited mechanical improvement 2. Hazardous chemicals 3. Not suitable for oxide removal	1. Ultra-smooth finish (R_a < 0.1 µm) 2. Shiny and clean 3. Enhanced corrosion resistance	[63-65]
ECM	1. Stress free, oxide free material removal 2. Suitable for complex shapes and smooth finishes	1. High power consumption 2. Complex control of gap and flow 3. Requires electrolyte handling	1. Burr free surfaces 2. Can achieve low R_a (0.2 to 0.5 µm) 3. No thermal damage or stress	[66,67]

Fundamentals of electrochemical machining

This overview indicates that anodization, PEO, and ECP are all primarily based on the oxide film growth or its stabilization. While such films can provide corrosion protection, they inherently lead to problems such as porosity, cracking, and nonuniform morphology. The film-forming techniques tend to passivate the surface rather than bring about marked refinement. In contrast, ECM is based on a quite different process in which low-valence pathways are controlled to induce anodic dissolution and, thereby, prevent passive film growth. This difference is important and suggests that ECM should not be regarded simply as another electrochemical technique, but rather as a complementary one. Whereas surface-modifying techniques add a film, ECM shapes the material itself, producing smooth, clean, and stress-free surfaces without thermal damage. For this reason, ECM is especially well adapted to generating robust, defect-free, and chemically active Ti6Al4V surfaces.

Although ECM is widely recognized as a technique that enables precise material removal and is often considered an advanced form of electrochemical etching, its primary mechanisms involve controlled anodic dissolution governed by defined thermodynamic and kinetic constraints. For alloys such as Ti6Al4V, this is not a single, uniform process but proceeds through multiple valence states (Ti^+, Ti^{2+}, Ti^{3+}, Ti^{4+}), each dictating whether the surface becomes passivated or remains oxide-free. ECM, in contrast to traditional methods, where surface treatments are performed by deliberately growing oxide films, methodically removes oxide films and controls surface dissolution. It is, therefore, provides a means of surface modification by dissolution at an atomic level. The differences between anodization, PEO, ECP, and ECM are presented schematically in Figure 1, where the key difference in ECM is the creation of a smooth, oxide-free surface through controlled, low-valence dissolution, in contrast to the film-based surface modification of the other techniques.

Understanding the fundamental mechanism of ECM requires investigating the dissolution pathways, along with the electrochemical reaction scheme governing the dissolution of titanium in aqueous electrolytes. This provides a basis for investigating the possibilities in which titanium atoms transition through variable ionic states, directly impacting surface smoothness, oxide formation, and overall ECM performance.

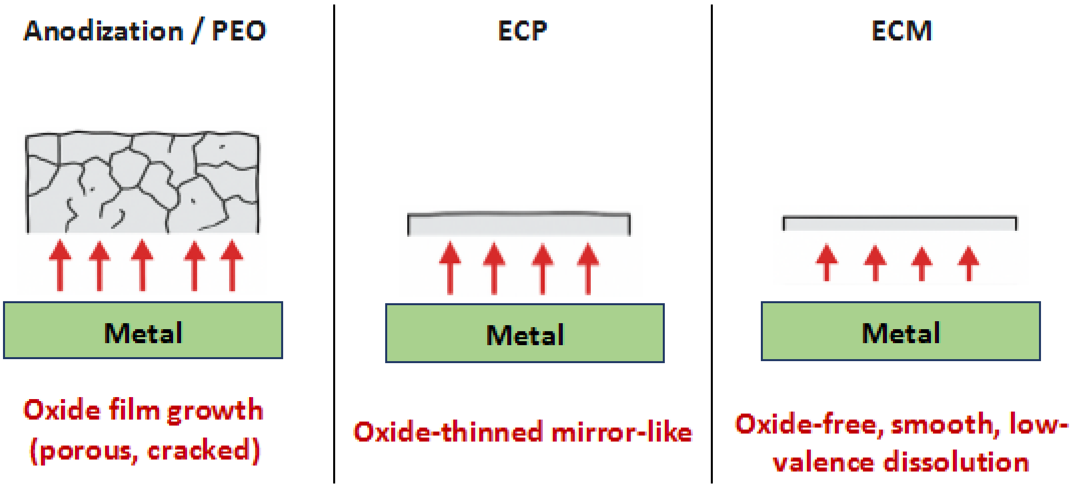


Figure 1. *Schematic comparison of electrochemical surface modification techniques*

Possible dissolution pathways in electrochemical machining

During the electrochemical dissolution of titanium, several oxidation states are possible, including Ti^{2+}, Ti^{3+}, and Ti^{4+}. Each of these paths directly affects whether the surface remains smooth and oxide-free or becomes passivated and roughened. In general, low-valence dissolution (Ti^+, Ti^{2+}) favours ionic solubility and a uniform surface texture, while higher-valence pathways promote oxide precipitation and passive film formation. Therefore, a valence-controlled ECM approach, particularly one that favours Ti^{3+} and Ti^{2+} over Ti^{4+}, represents a scientifically robust approach to surface finish. Strategic control of key process parameters, including applied potential, electrolyte composition, and current density, tunes the dissolution regime toward passive oxide suppression and improved finish predictability, thereby optimizing ECM for improved surface smoothness of Ti6Al4V.

Electrochemical reaction scheme

In aqueous NaCl solution, NaCl dissociates into Na^+ and Cl^- ions, while water splits into H^+ and OH^- ions as presented in Reaction (1) and (2) [68,69].

$NaCl \rightarrow Na^+ + Cl^-$ (1)

$H_2O \rightarrow H^+ + OH^-$ (2)

Upon applying an electric current, Na^+ migrates to the cathode and is reduced to Na, which reacts with water to form NaOH and H^+; simultaneously, H^+ is reduced to H_2 gas, as shown in Reactions (3) to (5).

Reactions at the cathode:

$Na^+ + e^- \rightarrow Na$ (3)

$Na + H_2O \rightarrow NaOH + H^+$ (4)

$2H^+ + 2e^- \rightarrow H_2$ (Hydrogen evolution) (5)

For the selected titanium alloy, Ti is oxidized to Ti^{2+} (Reaction (6)), which forms $TiCl_2$ and $Ti(OH)_2$ (Reactions (7) and (8)). $TiCl_2$ hydrolyses to $Ti(OH)_2$ (Reaction (9)), while Cl^- oxidizes to Cl_2 (Reaction (10)), forming $TiCl_3$ (Reaction (11)). Further reactions produce $Ti(OH)_3$ and $Ti(OH)_4$ (Reactions (12) and (13)), with HCl as a by-product (Reaction (14)) [70].

$Ti \rightarrow Ti^{2+} + 2e^-$ (6)

$Ti^{2+} + 2Cl^- \rightarrow TiCl_2$ (7)

$Ti^{2+} + 2(OH)^- \rightarrow Ti(OH)_2$ (8)

$2TiCl_2 + 4(OH)^- \rightarrow 2Ti(OH)_2 + 4Cl^-$ (9)

$4Cl^- \rightarrow 2Cl_2 + 4e^-$ (10)

$$\mathrm{2TiCl_2 + Cl_2 \rightarrow 2TiCl_3} \tag{11}$$
$$\mathrm{2Ti(OH)_2 + H_2O + O_2 \rightarrow 2Ti(OH)_3} \tag{12}$$
$$\mathrm{2TiCl_3 + 8(OH)^- \rightarrow 2Ti(OH)_4 + 6Cl^-} \tag{13}$$
$$\mathrm{H^+ + Cl^- \rightarrow HCl} \tag{14}$$

The reaction product, $TiCl_4$, forms at the workpiece interface as a stable, high-vapour-pressure compound. Under basic conditions, it hydrolyses back to $Ti(OH)_4$, hindering anodic dissolution [71]. In acidic media, however, the formation of $TiCl_4$ is favoured, which, depending on environmental conditions, for example, the presence of oxygen and water vapour, can further undergo oxidation and hydrolysis reactions [72].

These sequential reactions lead to the formation of TiO_2, active oxidation, and, eventually, the buildup of Na_2TiO_3 layers [73]. The full reaction pathway, including $TiCl_4$ formation, hydrolysis, oxidation, and layer formation, is illustrated in Figure 2.

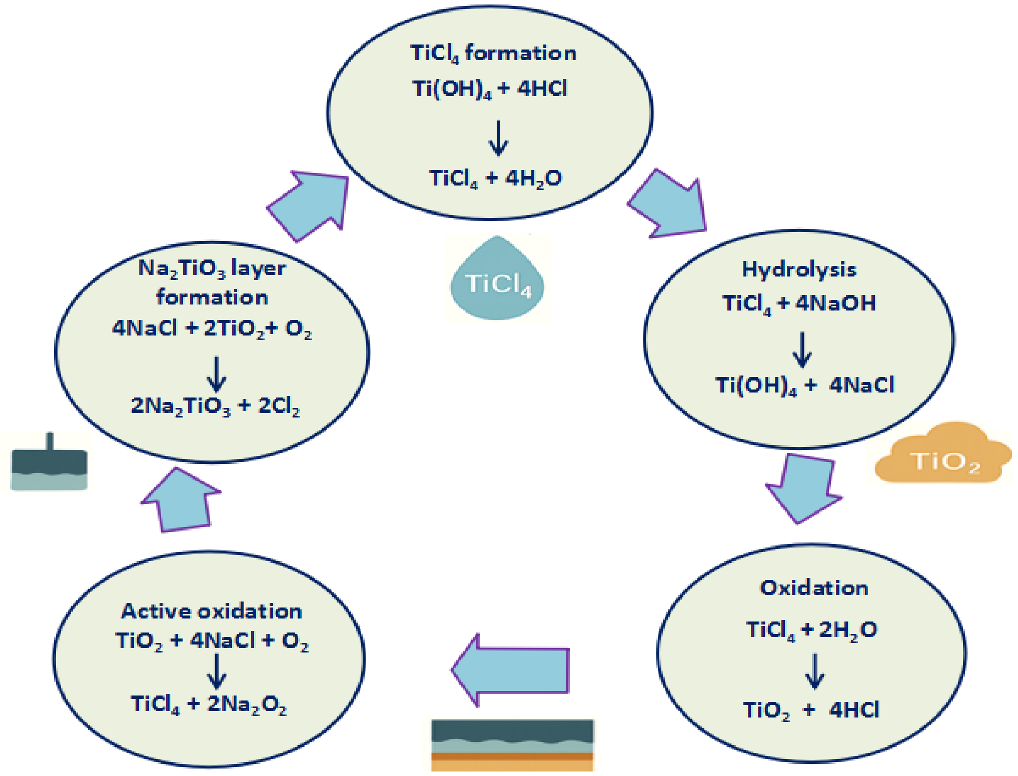


Figure 2. *Cyclic reaction mechanism showing $TiCl_4$ formation, hydrolysis, oxidation to TiO_2, and subsequent Na_2TiO_3 layer development during electrochemical dissolution of Ti6Al4V*

Influence of valence state on electrochemical dissolution

The surface morphology achieved during electrochemical dissolution is closely linked to the valence state of the dissolving titanium ions, as each valence state has a different dissolution pathway. Ti^{4+} species generally dominate at higher potentials and at acidic to neutral pH, where they readily hydrolyse to TiO_2 and other stable oxides, resulting in passivation, non-uniform dissolution, and salt precipitation, leading to a rough, defective surface. Therefore, a high-valence-dominated dissolution pathway is not desirable in precision surface engineering. In contrast, lower valence states such as Ti^{3+} and Ti^{2+}, and even at extreme cases of Ti^+, remain more soluble in aqueous electrolytes and suppress passive oxide precipitation [74]. This mechanistic difference is depicted in Figure 3, which shows that Ti^{4+}-dominated dissolution supports the growth of oxide films and a rough surface morphology, typical of passivation. On the other hand, dissolution dominated by lower-valence states ($Ti^{3+}/Ti^{2+}/Ti^+$) suppresses oxide accumulation, yielding atomically smooth, defect-free surfaces. Thus, the low-valence pathway enables the achievement of uniform surfaces with superior finish and dimensional accuracy, highly required for biomedical implants, aerospace components, and other high-performance applications [75].

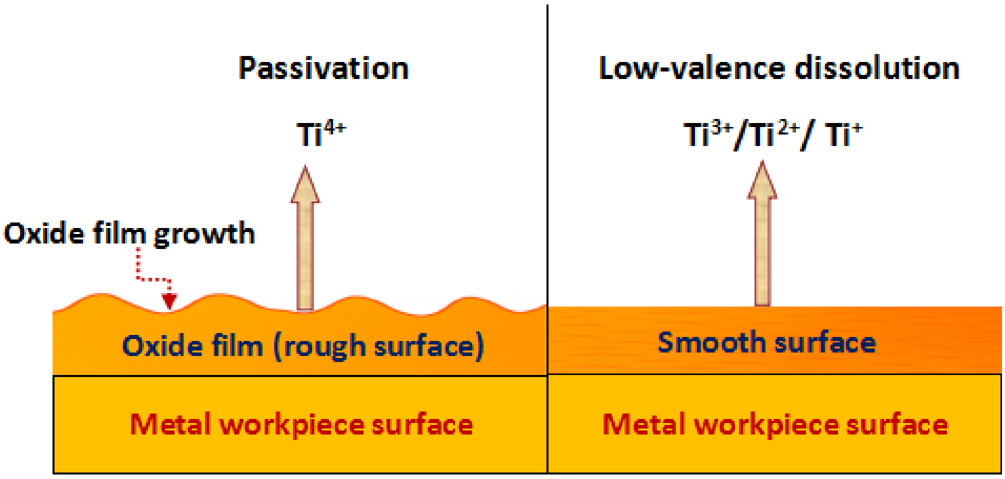


Figure 3. *Schematic showing* Ti^{4+} *induced passivation vs. low-valence* ($Ti^{3+}/Ti^{2+}/Ti^{+}$) *dissolution for surface smoothness*

Figure 4 shows the relationship between the valence state of titanium ions and key dissolution properties, such as the required electrode potential, surface smoothness, and oxide formation tendency.

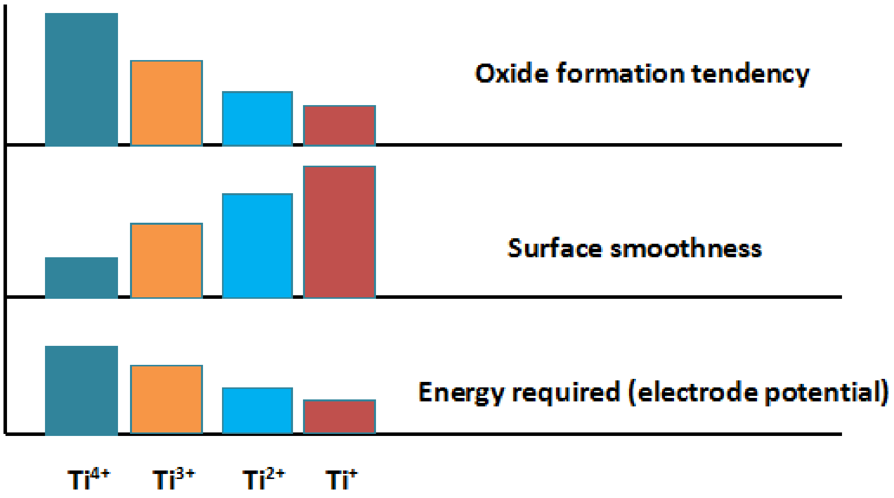


Figure 4. *Comparison of Ti ion valence states* Ti^{4+}, Ti^{3+}, Ti^{2+}, *and* Ti^{+} *based on oxide formation, surface smoothness, and energy requirement during electrochemical dissolution*

As demonstrated, lower valence states (Ti^{+}, Ti^{2+}) are associated with reduced oxide formation and enhanced surface smoothness, requiring lower electrode potentials compared to Ti^{3+} and Ti^{4+}. The concept of apparent valence is important for a better understanding of dissolution behaviour. Due to electrochemical conditions, the actual oxidation number of ions moving between the electrode and the electrolyte may differ from their theoretical valence. Applied potential, current density, and electrolyte composition are parameters that affect whether a metal dissolves in high-valence or low-valence states [76].

Role of process parameters in shaping dissolution pathways

Due to its pronounced tendency toward passivation, complex multivalent dissolution behaviour (from Ti^{2+} to Ti^{4+}), and relatively low electrical conductivity, titanium exhibits peculiarities in ECM compared to other metals. These make the anodic dissolution of titanium highly unstable and sensitive to process parameters; consequently, very smooth, oxide-free surfaces require precise control of potential, current, and electrolyte composition. Namely, these parameters will fix whether the pathways of titanium dissociation proceed via high-valence states, which promote passivation and surface roughening, or via low-valence states, yielding smooth, oxide-free surfaces. A deeper understanding of such mechanisms extends the possibility of transitioning ECM from a traditional material-removal process towards a precise surface modification. Within process variables, the applied potential exhibits the most influence since it controls the main electrochemical reactions directly and defines the thermodynamic limits of oxidation for titanium [77,78]. At high electrode potentials, titanium usually dissolves in Ti^{4+}, which hydrolyses to form a passive TiO_2 layer. Several studies have already shown that passive films formed at high voltages degrade surface quality [79]. However, lower voltages are sufficient to suppress the oxidation of the higher-valence titanium species and promote uniform dissolution [80,81]. Hence, the low-valence dissolution regime usually yields smoother titanium surfaces with reduced salt precipitates and enhanced morphological control in both contexts [82, 83].

Apart from the applied potential, electrolyte composition plays a very significant role in accomplishing improved electrochemical behaviour. Chloride-containing electrolytes such as NaCl or KCl, used in ECM processes form soluble $TiCl_x^{n-}$ complexes, which destabilize passive oxide films [84,85]. On the other hand, neutral salts like Na_2SO_4 or $NaNO_3$, the electrolytes keep more stable and less reactive ionic transport [86,87]. Hydrolysis equilibria can be further modified by the addition of organic inhibitors, pH modifiers, or chelators such as EDTA and oxalic acid, which keep titanium in low-valence, soluble states [88-90]. Novel mixed electrolytes incorporate organic modifiers such as ethylene glycol to control mass transport and mitigate runaway oxide growth during machining [91,92]. These electrolytes temper the anodic reaction and result in more uniform material removal by suppressing aggressive, Ti^{4+} driven passivation. Furthermore, advancements in electrolyte chemistry have allowed several authors to suppress localized pitting and improve dimensional accuracy in jet and micro-ECM of Ti6Al4V [93,94]. Considered collectively, these observations indicate that intelligent electrolyte design is an enabling factor for stabilizing low-valence dissolution pathways and generating smooth, oxide-free Ti6Al4V surfaces.

Current density is another important factor that intimately links mass transport with reaction kinetics. At moderate current densities, ionic migration and dissolution kinetics remain balanced, favouring steady low-valence dissolution pathways which result in smooth, defect-free surfaces [95]. However, high current densities promote Ti^{4+} oxidation and oxygen evolution, leading to localized precipitation, pitting, and hence surface instability [96]. Such a current regime compromises surface finish quality, besides increasing electrical load and thereby diminishing process sustainability. Many reports in the literature indicate that very high current densities accelerate oxygen evolution and salt precipitation, leading to localized pitting [97]. Very low current densities lead to unstable surface removal and poor machining consistency. Optimization of current density thus assumes importance not only to guarantee uniformity in low-valence dissolution but also to ensure dimensional accuracy and to avoid localized thermal or electrochemical instabilities [98].

The interplay among applied potential, current density, and electrolyte chemistry ultimately determines whether titanium dissolution proceeds via high-valence passivating pathways or low-valence active pathways. Figure 5 illustrates how the control parameters can shift the system from Ti^{4+} driven passivation and oxide growth to controlled dissolution mediated by Ti^{3+} or to low-valence pathways dominated by Ti^{2+}, where oxide-free, smooth surfaces are produced to enhance functional quality. Their combined influence discovers the evolution of Ti6Al4V surfaces from rough, passivated, and defect-prone to smooth, oxide-free, and functionally enhanced. ECM can be refined to more fully guide the surface of a test sample to desired thermodynamic conditions by balancing the parameters described, such as the use of $NaNO_3$-based electrolytes with electrolyte-added nanoparticles, moderate applied potentials to reduce the Ti^{4+} formation rates and controlling current density to avoid localized unstable ECM dissolution conditions. This is of great importance to the bio-medical field for biofilm-resistant and bio-compatible implants and for the aerospace industry, where components need to be defect-free for fatigue resistance and finish quality is critical [99,100].

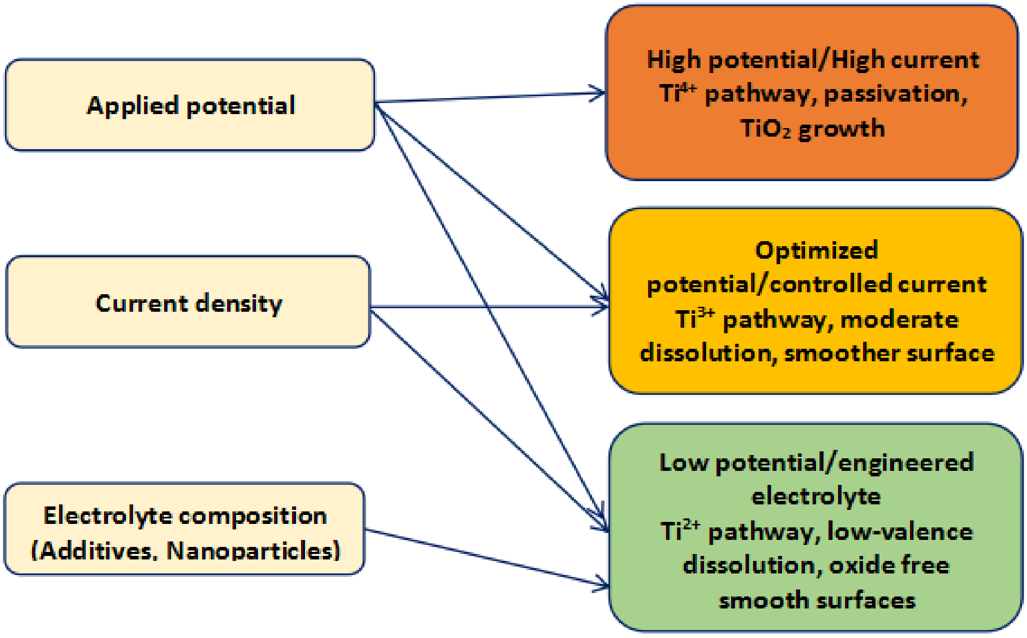
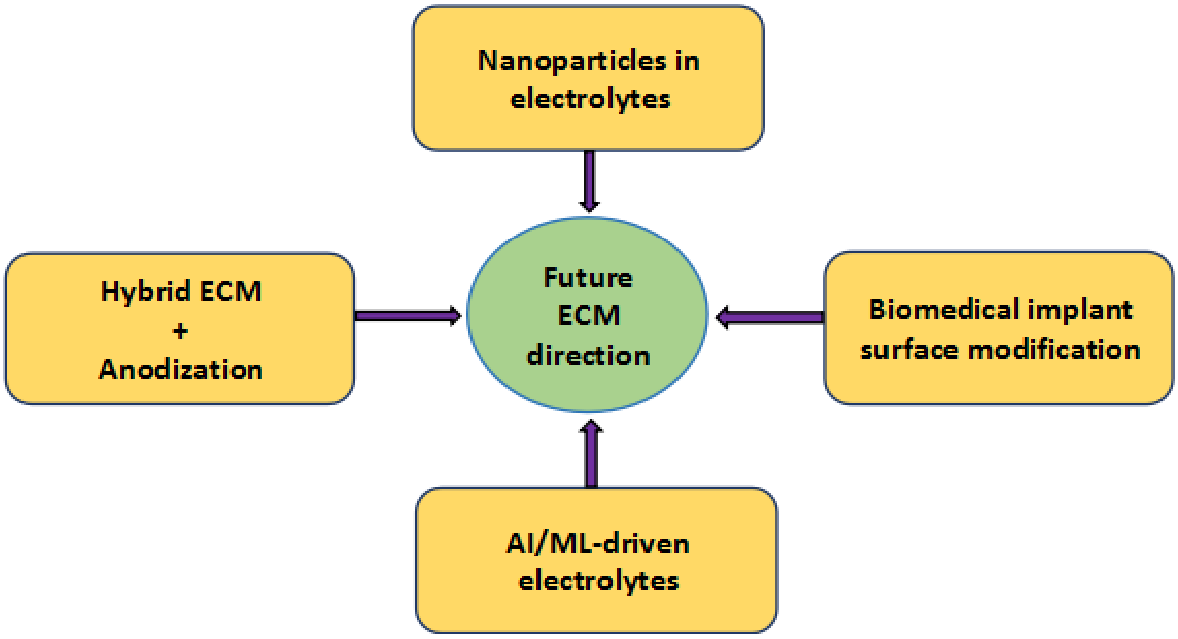


Figure 5. *Process parameters, dissolution map*

Future scope and research challenges in electrochemical machining

Numerous research challenges and future opportunities become more apparent as ECM evolves from a subtractive machining technique into a precision-controlled surface engineering tool. One of the most important requirements for Ti6Al4V and other titanium alloys is the development of adaptive control and real-time monitoring systems. Dynamic feedback loops that can control electrolyte chemistry, pH, ion concentration, and local temperature in situ are currently absent from ECM. Real-time control is necessary to avoid passivation and ensure smooth, oxide-free surfaces, since both factors directly influence whether titanium exists in low- or high-valence states [101]. Closed-loop regulation in ECM can be achieved using advanced sensors, such as optical probes, UV-visible spectroscopy, or electrochemical impedance spectroscopy (EIS), to deliver extremely stable and reproducible results [102]. Nanoparticle mixed electrolytes are opening new avenues to make ECM more precise and efficient. In this respect, nanoparticles of gold (AuNPs), and silver (AgNPs), and carbon-based nanomaterials such as graphene and carbon nanotubes (CNTs) have reported as distinguished additives due to their potential in alleviating surface passivation, stabilizing low-valence species, and enhancing charge transfer dynamics during dissolution [103]. Ceramic nanoparticles, such as SiC and Al_2O_3, similarly prevent microprecipitation, facilitate heat dissipation, and increase the local electrolyte conductivity for efficient dissolution. These developments support active electrolyte systems that guide electrochemical reactions along thermodynamically favoured dissolution pathways [104]. Also, integrating ECM with anodization may smooth the surface and remove oxides via valence-controlled dissolution. When applied sequentially or in parallel, these two techniques extend the chemical and structural diversity of surfaces by increasing mechanical integrity and functional plausibility [105]. The aim of this fusion will be to serve biomedical targets, especially in the design of implant surfaces processed via ECM that can inhibit biofilm development, reduce residual stresses, and maintain high biocompatibility. The exact relationship between multiphase reactions, alloy microstructure, and ion migration remains poorly explored. Such incompletely understood multiscale phenomena will be clarified in the near future by innovations in computational modelling, machine learning and optimization, in situ techniques with time resolution, and the integration of SEM, Raman, and XPS methods [106,107].

The approach enables transforming ECM from a conventional subtractive process into an intelligent, multifunctional surface-engineering platform for advanced applications. Some of these emerging strategies, as shown in Figure 6, include nanoparticle mixed electrolytes for enhanced catalytic dissolution, hybrid ECM-anodization methods for dual-functional surfaces, ECM-based treatments of implants in biomedicine and AI/ML-driven frameworks for intelligent process optimization. Merging these trends with hierarchical modelling and sensor integration will enable ECM to overcome the constraints of current state-of-the-art and to achieve next-generation surface modification strategies in biomedical, aerospace, and precision engineering.



Nanoparticles in electrolytes

Hybrid ECM + Anodization

Future ECM direction

Biomedical implant surface modification

AI/ML-driven electrolytes

Figure 6. *Future road-map diagram for ECM*

Conclusion

This review critically analyses electrochemical surface modification strategies for the Ti6Al4V alloy, with particular emphasis on positioning ECM as a valence-controlled dissolution process rather than solely a subtractive machining technique. Through this approach, passivation can be suppressed and smooth, oxide-free, and defect-free surfaces can be achieved by carefully adjusting the applied potential, the electrolyte composition, and the current density through controlled dissolution toward the lower valence states (Ti^+, Ti^{2+}, and Ti^{3+}). A comparative evaluation of electrochemical methods demonstrates ECM's unique advantages in terms of homogeneity, energy efficiency, and surface cleanliness, making it a complementary technique to the film-based approach. This conceptual framework first explores the variables that control dissolution channels and places ECM as a valence-selective, novel process. By considering ECM not as a subtractive machining process but rather as a platform for advanced surface engineering, it could offer a new path to improve Ti6Al4V surfaces for high-performance applications. The possibilities for ECM go far beyond the traditional approach.

Recent research focuses on the engineering of bioimplants from ECM that exhibit high Biocompatibility, remarkable wear resistance, and strong biofilm suppression. Besides, hybrid anodization techniques inspired by ECM would yield surfaces with multiple functionalities, while electrolytes infiltrated with nanoparticles would enhance catalytic dissolution and stabilize low-valence titanium. These improvements in precision can be used in microdevices, aerospace parts, and biomedical implants that require extremely smooth, stable surfaces. Real-time process monitoring, strategically designed electrolytes and machine-learning-driven control techniques will most likely expand these new ECM capabilities. The ability of ECM to control biofilm by valence dissolution places it as the pioneering technique for next-generation surface modification of titanium alloys for demanding engineering and biomedical applications.

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