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ABSTRACT

Titanium and its alloys are widely utilized in various fields, such as biomedical and aerospace, and in other industrial applications. However, its surface modification is essential to further enrich its properties to enhance its effectiveness. Researchers across the globe are continuously working on a variety of surface modification methods to enhance the properties of titanium and its alloys. This paper presents a comprehensive review of surface modification methods utilized for titanium and its alloys. Some of the important modification techniques discussed in this paper includes mechanical, chemical, electrochemical, thermal, and physical surface modification methods. This paper also provides insights into surface modification methods in terms of improving corrosion and wear resistance, biocompatibility, and hardness of titanium and its alloys.

I. INTRODUCTION

Titanium has been recognized for over two decades as one of the most widely available structural metals, second only to magnesium, iron, and aluminum.[1] The alloying of titanium with different elements leads to the formation of various titanium alloys, which exhibit comparable or superior properties to commercially pure titanium (CP-Ti).[2] Among these, NiTi alloys are particularly valued for their applications in aeronautics, automotive, and biomedical fields, while Ti_2AlNb alloys demonstrate significant potential in advanced automotive and aerospace sectors.[3,4] These titanium alloys are classified into three primary types: α-alloys, β-alloys, and α + β alloys. The properties of these alloys are largely determined by their microstructure, which in turn depends on their chemical composition and thermomechanical processing.[5] Titanium alloys have garnered increasing attention over the past decade due to their exceptional biocompatibility, high specific strength, excellent corrosion resistance, and stability across a wide range of temperatures. These characteristics make them suitable for a variety of engineering applications,[6–8] including aerospace, medical, and general industry.[9] Furthermore, additively manufactured Ti-6Al-4V has shown great potential across a broad spectrum of industrial applications.[10]

However, despite their remarkable properties, titanium alloys often require surface modification to address limitations related to biocompatibility, adhesion, and corrosion resistance, particularly for use in specialized fields. For example, the widely used titanium alloy Ti-6Al-4V is restricted in tribological applications due to its low surface hardness, high friction coefficient, and poor abrasive wear resistance.[11] Titanium's role as a key material for orthopedic and dental implants is notable, but surface modification is necessary to enhance durability and antibacterial properties.[12] Surface modification of titanium alloys is especially crucial in biomedical applications, where it improves corrosion and wear resistance, biocompatibility, and implant bonding to bone tissue. This process also enhances mechanical fastening and bone inductivity and conductivity, and it reduces healing time post-implantation.[13,14] Moreover, the addition of palladium components can modify the intermetallic compound (IMC) morphology of hybrid solder junctions, changing it from granular to a columnar rod shape.[15] Therefore, it is essential to understand the advantages of surface modification on titanium alloys, both in terms of property enhancement and technological applications. This paper provides an in-depth review of titanium alloy surface modification methods, demonstrating how these techniques improve mechanical, tribological, and biological performance.[16] The subsequent sections discuss the various surface modification methods in detail.[17]

A. Methods of surface modification of titanium and its alloys

The modification techniques can be categorized into mechanical, chemical, electrochemical, and thermal methods. In addition, combining two or more of these techniques, often referred to as hybrid or mixed treatments, typically results in improved material properties.[12]

1. Mechanical based surface modification

In this process, mechanical forces are applied to alter the surface topography of the material. The techniques involved include machining, grinding, polishing, and blasting.[18,19]

Although machining is not traditionally classified as a surface modification technique, it has been effectively utilized for creating specific surface features in implants for many years. Machining can generate well-defined surface topographies, clean the surface, or increase roughness, thereby enhancing bonding adhesion.[20,21] The periodic grooves on implant surfaces are dependent on factors such as the type of machining equipment, the cutting tool, and the tool's cutting angle relative to the implant material.[22] Figure 1 shows a scanning electron micrograph of a machined implant surface.

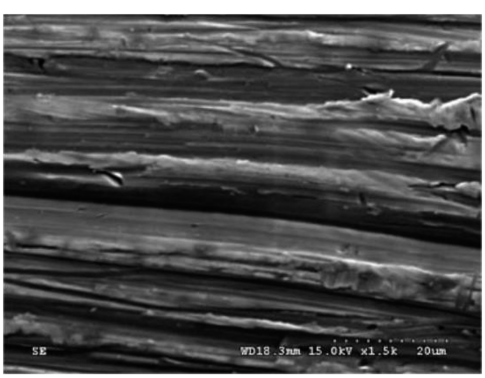

FIG. 1. Scanning electron micrograph showing periodic grooves of a machined implant surface.[22] [Reproduced with permission from Coelho *et al.*, J. Biomed. Mater. Res. **88**(2), 579–596 (2009). Copyright 2009 Wiley].

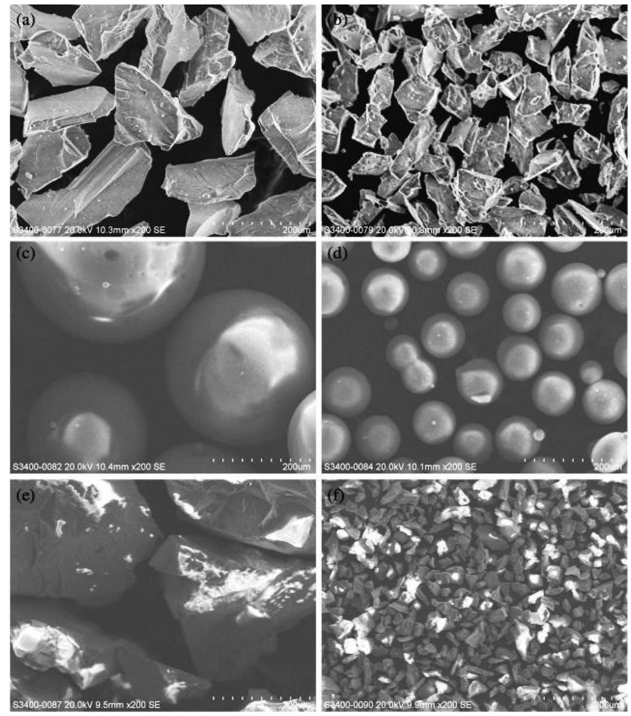

FIG. 2. SEM micrographs of blasting materials: (a) 110 μm diameter Al_2O_3 powder; (b) 50 μm diameter Al_2O_3 powder; (c) 150–300 μm diameter glass beads; (d) 45–75 μm diameter glass beads; (e) 250 μm diameter aluminum grits; (f) 44 μm diameter aluminum grits.[24] [Reproduced with permission from Guo *et al.*, Silicon **11**, 2313–2320 (2019). Copyright 2019 Springer Nature].

After machining, the titanium implant surface typically undergoes grit-blasting, a process where abrasive particles ranging from 110 to 250 μm, such as aluminum oxide (Al_2O_3), silicon oxide (SiO_2), or titanium oxide (TiO_2), are directed at the material surface.[23] Guo *et al.*[24] investigated the effects of different abrasives, including Al_2O_3, SiO_2 glass, and aluminum metal grits, on surface roughness and contamination of titanium implants. Their study suggested that Al_2O_3 may be the most suitable abrasive for sandblasting titanium dental implants. The various abrasive materials used in the experiments are shown in Fig. 2.[24]

Al_2O_3 is frequently used as an abrasive blasting medium; however, it often remains adhered to implant surfaces even after extensive cleaning protocols, including ultrasonic cleaning, acid passivation, and sterilization. The release of these adhered particles into surrounding tissues and their interference with the osseointegration process of the implant have been well-documented.[25]

2. Chemical and electrochemical based surface modification

In chemical-based surface modification, chemical reactions occur between titanium, its alloys, and the solution, improving biocompatibility, bioactivity, bone conductivity, and corrosion resistance while removing surface contaminants.[26–28] Common techniques for surface treatment include sol–gel methods, anodic oxidation, chemical vapor deposition (CVD), and chemical treatment.

Anodizing, an electrochemical method, promotes the formation of a micrometric oxide layer by optimizing current or potential. Visai *et al.*[29] utilized Anodic Spark Deposition (ASD), an electrochemical technique, in a calcium phosphate-enriched solution to modify the surface morphology, chemical composition, and structural properties of titanium. The resulting titanium oxide layer, with enhanced calcium content, anatase structure, and microporous surface, offers potential for controlling bacterial adhesion and improving tissue integration. In addition, the higher calcium content suggests aesthetic advantages for abutment treatment in the transmucosal region. Figure 3 shows SEM micrographs of untreated and ASD-treated titanium samples.[29]

Kesik *et al.*[30] investigated the impact of alkali treatment on anodized samples of titanium alloys, specifically Ti-15Mo, Ti-13Nb-13Zr, and Ti-6Al-7Nb. Their findings revealed that alkali-treated surfaces formed a porous oxide layer, enhancing bioactivity. Electropolishing effectively removed surface imperfections, resulting in a smoother surface with reduced roughness than untreated surfaces.[31] Safwat *et al.*[32] successfully produced a protective TiO_2 layer through anodization of Ti-6Al-7Nb and Ti-6Al-4V alloys using a 10% oxalic acid solution for 30 s at 20–80 V. An optimal anodization voltage of 40 V yielded a stable oxide layer with excellent corrosion resistance, making it suitable for biomedical applications. Prando *et al.*[33] concluded from their experimental investigation that electrochemical anodization of pure titanium significantly enhances corrosion resistance. They observed improved corrosion protection in chloride- and fluoride-containing solutions, with a compact, almost amorphous oxide layer forming at lower voltages (<40 V) that exhibited superior corrosion resistance.

The electrochemical decontamination technique, operating at a low alternating potential, effectively cleans the titanium surface without compromising its structural integrity. By utilizing a combination of cathodic and anodic potentials, it efficiently removes salivary contaminants and supports biofilm formation when combined with mechanical brushing.[34] Figure 4 presents Scanning Electron Microscopy (SEM) images showcasing the morphology of treated titanium surfaces.[34] The enhanced biocompatibility and favorable conditions for cell growth can be attributed to HF treatment, which introduces micro- and nano-scale topographies, along with the presence of fluoride, hydride, oxide, and reduced hydrocarbon content.[35] This method is widely used for depositing thin, corrosion-resistant layers and is advantageous for uniformly coating complex geometries on substrates.[36]

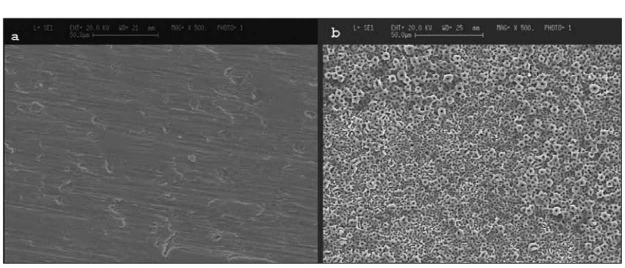

FIG. 3. SEM micrograph of a (a) non-treated titanium (Ti) and (b) ASD treated titanium sample.[29] [Reproduced with permission from Visai *et al.*, J. Appl. Biomater. Funct. Mater. **6**(3), 170–177 (2008). Copyright 2019 Sage Publications].

Chemical vapor deposition (CVD) is a robust technique for producing high-quality thin films and coatings.[37] CVD methods are classified based on the energy source used in the reactor for thin film deposition. Common methods include hot-wall CVD, cold-wall CVD, and plasma-enhanced CVD (PECVD). In hot-wall CVD, the chemical reactions and deposition occur directly on the substrate within a reactor surrounded by heating elements, providing the required temperature for the reaction. In cold-wall CVD, only the substrate is heated, either by electric current or induction, while the chamber walls remain at ambient temperature. PECVD involves introducing a mixture of precursor gases, such as hydrocarbons and hydrogen, into a vacuum chamber containing a substrate.[38] Plasma is generated in the gas mixture via microwave or radio frequency, causing the precursor molecules to dissociate into reactive species, which then react and deposit onto the substrate, forming a thin film.[39]

The dispersion of silver nanoparticles on Ti-6Al-4V and its modified titanium alloy (Ti-6Al-4V/TNT) via Chemical Vapor Deposition (CVD) using the precursor $[Ag_5(O_2CC_2F_5)_5(H_2O)_3]$ enhances surface free energy, Young's modulus, surface roughness, and hydrophobic properties.[40] Figure 5 illustrates the results of scratch testing on Ti-6Al-4V/TNT5 coating and Ti-6Al-4V/TNT5/AgNP composite, where Ft represents the friction force, Fn the normal force, Lc the critical load, and Lf the critical friction force.[40] The application of diamond films on titanium substrates via microwave-plasma CVD is expected to promote effective osseointegration for diamond-coated implants.[41]

The sol–gel process, a chemical method for producing inorganic materials such as coatings, glasses, and ceramics, involves transitioning a liquid solution into a gel.[42] This technique offers advantages such as enhanced uniformity, higher purity, lower processing temperatures, thinner coatings, and a cost-effective, user-friendly preparation process.[43] Jaafar *et al.*[44] optimized the sol–gel method to deposit a hydroxyapatite (HA) layer on Ti-6Al-4V, utilizing intermediate titanium dioxide layers to produce crack-free hydroxyapatite films with improved adhesion and coating integrity. This resulted in a significant increase in adhesive strength, and the HA/titania-coated samples exhibited excellent protective properties and low corrosion rates, indicating their suitability for bone replacement coatings. Catauro *et al.*[45] also applied the sol–gel process to synthesize HA, which was then coated on titanium disks. The results from WST-8 analysis show that HA systems produced through the sol–gel method are highly effective for modifying titanium implant surfaces and improving biocompatibility.

3. Laser based surface modification

Surface enhancement is crucial for improving the service functionality and longevity of metallic components in complex service environments in varied industrial domains.[46] Compared to traditional mechanical/chemical processes, laser surface modification has several appealing qualities and can be accomplished much faster and with greater repeatability.[47] Laser energy is used as the heating source in the Laser Surface Treatment (LST) process. Shock peening, engraving, selective laser melting, sintering, glazing, cladding, and surface alloying are examples of LST processes.[48] Many researchers have adopted different laser processes, such as shock peening,[49,50] engraving,[51,52] selective laser melting,[53,54] sintering,[55] cladding,[56] texturing,[57,58] and laser welding,[59,60] for material processing.

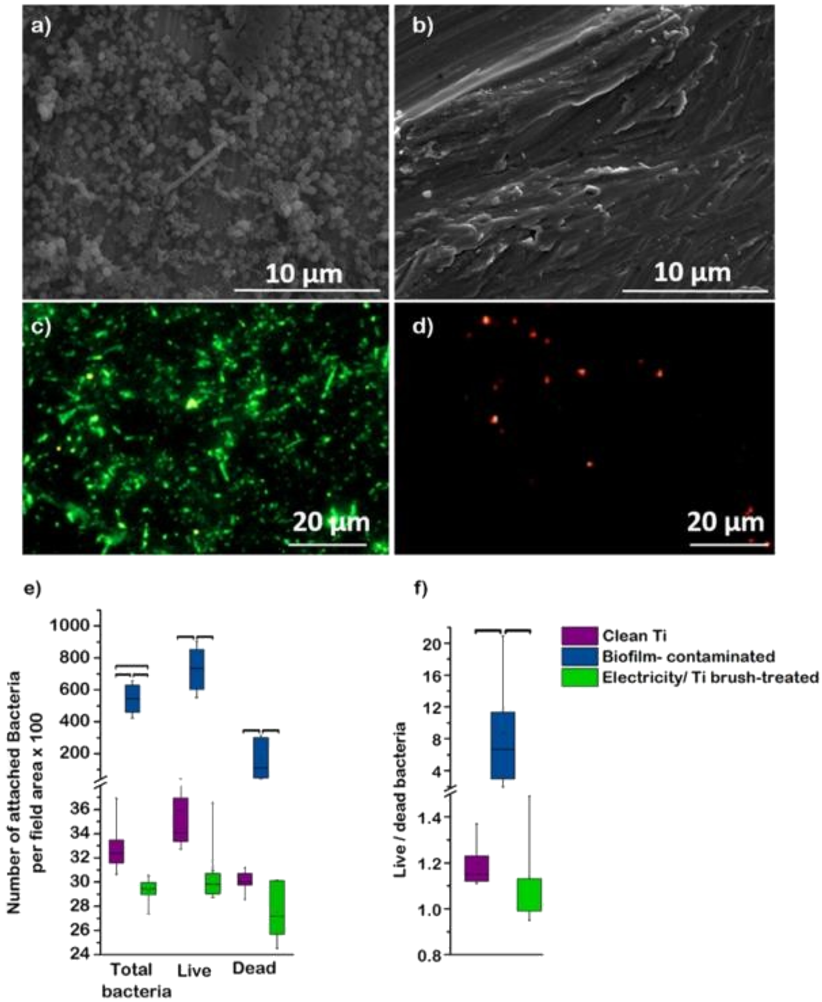

FIG. 4. (a) and (b) SEM images depicting the morphology of Ti surfaces: (a) Ti surface contaminated with biofilm; (b) surface after decontamination. (c) and (d) Fluorescence images with live/dead staining to show bacteria on the Ti surface before and after decontamination; green represents living bacteria, and red indicates dead or inactivated bacteria. (e) and (f) Comparison of the number of attached bacteria (per field area of 0.15 mm^2) and the viability (live/dead ratio) on Ti surfaces before and after biofilm contamination and subsequent decontamination. Eight discs were utilized for each group.[34] [Reproduced with permission from Al-Hashedi *et al.*, ACS Biomater. Sci. Eng. **2**(9), 1504–1518 (2008). Copyright 2016 American Chemical Society].

Laser texturing of Ti-6Al-4V ELI alloy and microgroove modifications depict reduction in wear with an increase in microhardness of 15% more than it had been before. When lubricated, a reduction of 29% in wear volume and a 26% reduction in friction coefficient were obtained compared to the untextured surfaces.[61] Figure 6 depicts the laser micromachining system and laser beam impact on the solid matter.[61]

With improved hydrophobic qualities and less surface wear, laser textured titanium surfaces show encouraging potential to improve titanium implant performance.[62] Figure 7 depicts the contact angle measurement of the titanium surface before and after laser modification.[62]

Femtosecond laser microtopography coatings applied to titanium implants have shown significant potential for developing microtopographic surfaces that enhance antibacterial properties while maintaining adequate biocompatibility.[63] The use of picosecond pulsed laser ablation to create mesh-type surface textures on pure titanium resulted in increased hydrophilicity, positively influencing the biocompatibility of bone marrow stem cells (BMSCs).[64] In addition, the periodic surface structure produced on Ti-6Al-4V through laser texturing combined with heat treatment exhibits superhydrophobic characteristics, as well as improved micro-hardness and erosion resistance, compared to untreated surfaces.[65]

4. Physical surface modification

In physical surface modification, the ultrastructure of the surface is modified through exposure to high-energy phenomena such

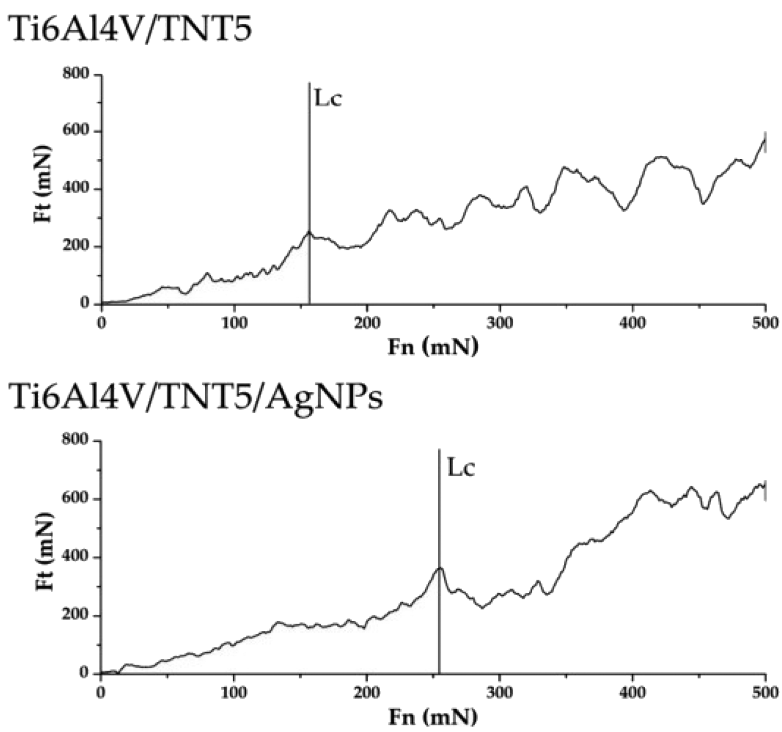

FIG. 5. Scratch test result: Ti-6Al-4V/TNT5 coating and for Ti-6Al-4V/TNT5/AgNP composite.[40] [Radtke *et al.*, Int. J. Mol. Sci. **19**(12) 3962 (2018); licensed under a Creative Commons Attribution (CC BY) license].

as charged particles, flames, or plasma. This method is characterized by its cost-effectiveness and simplicity. The techniques involved in physical surface modification include (i) plasma spray technology, (ii) plasma immersion ion implantation, (iii) plasma immersion ion implantation and deposition, and (iv) physical vapor deposition.[66] The plasma surface modification technique has garnered considerable attention in the field of biomedical engineering due to its efficient and economical surface processing capabilities across various materials.[67] In plasma spraying, a high-temperature plasma jet is utilized to melt and atomize a feedstock introduced into the plasma flame, typically resulting in protective and performance-enhancing coatings.[68] Kotian *et al.*[69] conducted an investigation into the impact of plasma working gas on the hydroxyapatite (HA) coating applied to titanium and Ti-6Al-4V alloys, focusing on its composition, crystallinity, and microstructure. The findings indicate that the plasma gas atmosphere significantly influences the composition,

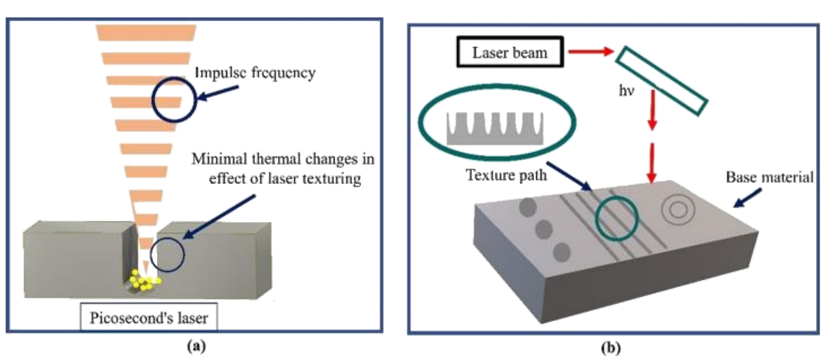

FIG. 6. (a) Laser micromachining system; (b) impact of laser beam on solid matter.[61] [Woźniak *et al.*, Arch. Civil Mech. Eng. **24**(3), 146 (2024); licensed under a Creative Commons Attribution (CC BY) license].

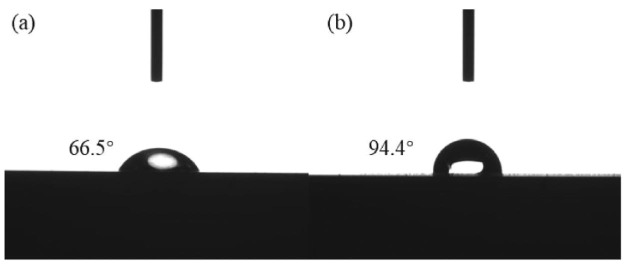

FIG. 7. Contact angle measurement of the titanium surface before and after laser modification.[62] [Hou *et al.*, Coatings, **14**(4), 516 (2024); licensed under a Creative Commons Attribution (CC BY) license].

crystallinity, and microcracking of dental implants coated with HA. In comparison to argon–hydrogen and nitrogen–hydrogen, the plasma gas atmosphere of argon and nitrogen exhibited the highest level of crystallinity. In addition, it is essential to control the plasma gas temperature to reduce the occurrence of microcracks resulting from thermal stress. Plasma immersion ion implantation is a surface modification technique wherein the target is enveloped by plasma, allowing ions to be implanted onto the surface, thus facilitating a quicker and more cost-effective treatment.[70] This method modifies the surface without affecting the bulk properties of the alloys and metals.[71] As the temperature increases (400, 500, and 600 °C), the surface roughness, corrosion resistance, and formation of TiO rutile enhance. At the highest temperature (600 °C), MG-63 cell activity improves, and a reduction in the viability of monotypic microbial biofilms is noted when the titanium surface is treated with ion implantation via immersion in oxygen plasma.[72] The implantation of silver (Ag) ions using the plasma immersion ion implantation technique on Ti-6Al-4V has shown enhancements in friction, wear, and corrosion resistance.[73] Physical vapor deposition (PVD) methods, including evaporation, sputtering, and ion plating, enable thin film deposition that enhances biocompatibility, corrosion resistance, bioactivity, and wear resistance.[74]

II. SUMMARY

The objective of this work is to perform a thorough review of various surface modification techniques aimed at enhancing the surface properties of titanium and its alloys. These properties are crucial across industries such as manufacturing, aerospace, and biomedicine. The review covers a range of surface modification strategies, including thermal and physical modification techniques, chemical and electrochemical methods, and mechanical treatments. Each of these methods has the potential to improve surface properties significantly, including hardness, biocompatibility, and resistance to wear and corrosion. The findings suggest that surface modification of titanium and its alloys is vital for optimizing titanium-based materials in challenging environments.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ishwer Shivakoti: Conceptualization (equal); Data curation (equal); Investigation (equal); Writing – original draft (equal). **Abhijit Bhowmik**: Conceptualization (equal); Methodology (equal); Supervision (equal); Writing – review & editing (equal). **A. Johnson Santhosh**: Funding acquisition (equal); Investigation (equal); Project administration (equal); Visualization (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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