



## SURFACE MODIFICATION OF TITANIUM ALLOYS Ti-6Al-4V AND Ti-6Al-7Nb: METHODS FOR ENHANCING WEAR RESISTANCE AND BIOCOMPATIBILITY. A BRIEF REVIEW

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### ABSTRACT

*Titanium and its alloys, primarily Ti-6Al-4V and Ti-6Al-7Nb, are widely used in various high-tech sectors due to their excellent mechanical properties, high corrosion resistance, and low density. However, these materials exhibit low wear resistance and a tendency to gall during friction, limiting their applicability in aggressive environments or under heavy loads. This review discusses the main challenges associated with the tribological properties of titanium alloys and various modern surface modification techniques, including chemical and electrochemical methods, laser coatings, ion implantation, and nanocoatings. The advantages of these techniques in improving wear resistance are analyzed, with a focus on applications in aerospace and medicine. Special attention is given to the impact of friction in different environments and the anti-friction properties of titanium alloys. The review highlights the need for further development of surface modification technologies to enable broader use of titanium and its alloys in extreme conditions and to extend their service life.*

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## 1. INTRODUCTION

Titanium alloys hold a significant position in modern industry due to the unique properties they offer. They combine high strength, low density, excellent corrosion resistance, and good biocompatibility, making them preferred materials for use in a range of high-tech industrial sectors.

Alloys such as Ti-6Al-4V, Ti-6Al-4V ELI, and Ti-6Al-7Nb are widely used in the production of critical components in fields like aerospace, aviation, and biomedicine. Specifically in medicine, these alloys are the material of choice for manufacturing implants and orthopedic devices due to their excellent compatibility with human tissue and long-term durability [1].

Despite their advantages, titanium alloys have certain limitations related to their low wear resistance and tendency to gall under friction. This characteristic leads to premature wear, particularly in dry friction conditions, affecting components and assemblies [2].

To overcome these limitations and enhance the performance of titanium alloys, various surface modification methods are applied. The most commonly used surface modification techniques for titanium alloys include nitriding, oxidation, surface alloying, ion implantation, and thermochemical treatment. These methods aim to optimize the mechanical properties and improve the biocompatibility of titanium alloys by creating surface layers that make them more suitable for specific

applications requiring high durability and safety standards [3].

This article reviews the most commonly used surface modification methods for Ti-6Al-4V and Ti-6Al-7Nb alloys, focusing on their effect on the wear resistance and biocompatibility of these alloys.

## 2. EXPOSITION

### Characteristics of Ti-6Al-4V and Ti-6Al-7Nb Titanium Alloys

The Ti-6Al-4V and Ti-6Al-7Nb alloys are the most commonly used titanium alloys for structural and biomedical applications. They are classified as  $\alpha+\beta$  titanium alloys, known for their excellent combination of mechanical strength, low density, and good corrosion resistance. These alloys are widely used in the aerospace industry and biomedicine due to their high specific strength and compatibility with biological tissues. Ti-6Al-4V is the most popular titanium alloy, characterized by good machinability, high fatigue resistance, and excellent corrosion resistance, especially in aggressive environments [4-6]. The Ti-6Al-7Nb alloy was developed as a biomedical alternative to Ti-6Al-4V, replacing the beta-stabilizing element vanadium (V) with niobium (Nb) due to vanadium's cytotoxicity in the body, making Ti-6Al-7Nb safer. Additionally, the Ti-6Al-4V ELI alloy has been developed with reduced vanadium content [7-9].

Despite their superior mechanical properties and corrosion resistance, these titanium alloys lack sufficient

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wear resistance, especially in contact friction with other surfaces. This drawback leads to premature wear of parts, which is a significant problem in biomedical implants and prostheses, where wear can result in particle formation that causes inflammatory reactions and implant rejection. Furthermore, although these alloys are considered biocompatible, their surface characteristics, such as roughness and chemical composition, can affect cellular adhesion and interaction with biological tissues. To improve these key properties, various surface modification techniques are used to increase wear resistance and improve interactions with biological systems [10-13].

The average static coefficient of dry friction for titanium alloys as Ti-6Al-4V is about 0.61, while the dynamic coefficient varies between 0.47 and 0.49 at a friction speed of 1 cm/s [14]. These values highlight the need for additional surface modification methods to minimize friction and enhance the material's wear resistance.

The friction problem with titanium alloys stems from their inherent properties, including high plasticity and low thermal conductivity. These factors lead to easy surface galling and an increased tendency of seizure. During friction, especially under higher loads, the contact points between surfaces can undergo plastic deformation, accumulating gases like oxygen and nitrogen, which further harden the contact zones [13-15]. This worsens the material's wear resistance and accelerates degradation.

While using  $\alpha$ - and  $\beta$ -stabilizers in alloying and various heat treatment methods can partially improve titanium's mechanical properties, they are insufficient to prevent galling under extreme conditions. The onset of this process depends on factors such as friction speed, load, the type of contact surfaces, and the environment where the friction occurs [16].

Depending on the environment, friction has different impact on the properties of titanium alloys. Experimental studies show that friction in environments with high humidity, seawater, or other fluids can initiate additional corrosion processes and increase wear further. The heat generated due to friction accelerates plastic deformation and promotes diffusion and oxidation processes [16].

Dry friction in an atmospheric media, such as in contact with air, increases surface wear of Ti-6Al-4V, which is related to the diffusion of oxygen and nitrogen into the contact points. These gases increase the hardness of the surface layer, which leads to severe wear and surface galling [17].

Research on Ti-6Al-4V shows that the wear intensity is highest when friction occurs in oil, followed by water containing 3% NaCl, with the lowest wear observed in dry air environment. Under these conditions, the depth of the galled layer can reach up to 30  $\mu\text{m}$  in air and 20  $\mu\text{m}$  in oil [18].

Friction in an argon media, which is an inert gas, significantly reduces wear of titanium alloys, preventing oxidation and diffusion processes. This is particularly useful for applications requiring minimal wear under high temperatures and loads, such as in aerospace engines and space technologies [19].

### Surface Modification Methods

The most commonly used surface modification methods for titanium alloys Ti-6Al-4V and Ti-6Al-7Nb are summarized in Table 1.

## 1. Chemical and Electrochemical Modification

The most common category of surface modification methods for titanium alloys involves chemical or electrochemical treatments. Chemical methods such as acid treatment or alkaline activation remove contaminants and oxides from the surface while promoting the formation of a durable oxide layer [20]. Electrochemical polishing, on the other hand, reduces micro-roughness and creates conditions for a lower friction coefficient and better wear resistance [21]. These processes are essential in biomedical applications where the modified surfaces must have high biocompatibility and corrosion resistance [22].

**Table 1** Surface modification methods for titanium alloys Ti-6Al-4V and Ti-6Al-7Nb, focusing on techniques that enhance wear resistance and biocompatibility

Surface modification methods	Chemical and electrochemical	Improve corrosion resistance and biocompatibility
	Anodizing	Creates a protective oxide layer enhancing corrosion resistance and wear properties
	Nitriding	Increases hardness and wear resistance by forming a hard titanium nitride layer
	Thermochemical Treatment	Enhances surface hardness and improves tribological properties
	Laser Modification	Applies wear-resistant materials precisely, enhancing durability
	Ion Implantation	Increases surface hardness, extending the life of implants
	Nanocoatings	Provide advanced tribological properties, improving integration with bone tissue

## 2. Nitriding

Nitriding of titanium alloys Ti-6Al-4V and Ti-6Al-7Nb is one of the most effective methods for increasing their wear resistance and hardness. The process involves nitrogen diffusion into the surface layer of the alloys at high temperatures or through ion nitriding in a plasma environment. As a result, a hard titanium nitride layer (TiN) is formed, significantly improving the surface properties. This layer provides much higher wear resistance and resistance to galling under friction, which is especially important for applications involving dynamic loading and friction in biomedical implants and aerospace components. Additionally, nitriding improves the corrosion resistance of titanium alloys without negatively affecting their biocompatibility, making it suitable for medical applications where materials need to be compatible with human tissue.

## 3. Anodizing

Anodization of titanium alloys is a widely used surface modification method that creates a thin, hard oxide layer (typically  $\text{TiO}_2$ ) on the metal's surface. This process is carried out through an electrochemical reaction, where the titanium alloy is immersed in an electrolyte and subjected to an electric current. The anodized layer significantly enhances corrosion resistance, protecting the base material from aggressive environments, including physiological fluids in biomedical applications. Moreover, the oxide layer improves wear resistance and can reduce the friction coefficient, which is particularly important for components subjected to friction and contact. In biomedicine, anodizing is used to improve the biocompatibility of titanium alloys

by providing a favorable surface for cellular adhesion and osseointegration.

#### 4. Thermochemical Treatment

Thermochemical treatment of Ti-6Al-4V and Ti-6Al-7Nb involves enriching the material's surface with chemical elements such as nitrogen, carbon, or boron through diffusion at high temperatures. Common techniques include nitriding and carbonitriding, which form surface layers with high hardness, wear, and friction resistance. These methods create thin but extremely hard layers, like TiN and TiCN, which significantly improve the wear resistance of titanium alloys without compromising their internal strength and ductility. Thermochemical treatment also enhances corrosion resistance and provides better tribological properties, which is important for applications such as engine components and biomedical implants. Applying these methods can improve the biocompatibility of titanium alloys by reducing the risk of adverse reactions in the body.

#### 5. Laser Modification

Laser coating is a modern surface modification technique that allows precise application of thin layers of wear-resistant materials onto titanium alloys [23]. Laser processing is used to create hard layers of carbides, nitrides, or oxides, which significantly increase the wear resistance and improve the tribological properties of titanium alloys [24]. This method is particularly effective in applications where high wear resistance and corrosion resistance are critical, such as in dental medicine or artificial joints [25]. Laser technologies enable precise control over the coating's thickness and composition, which is essential for achieving optimal properties for various applications [23-26]. For example, laser modification of Ti-6Al-7Nb significantly increases wear resistance without compromising the biocompatibility of this alloy [27].

#### 6. Ion Implantation

Ion implantation is a process in which ions of nitrogen or other chemical elements are accelerated and "implanted" into the surface of titanium alloys [28]. This leads to the formation of nitrides or carbides in the surface layer, improving the hardness and wear resistance of the titanium alloy [29]. Nitrogen ion implantation, for example, is particularly effective in alloys like Ti-6Al-4V, where increased surface hardness can reach values above 1000 HV [28-30]. This method is widely used in medical and industrial applications where friction resistance requirements are particularly important [30-31]. Ion implantation can extend the lifespan of titanium implants and reduce the risk of infections and adverse reactions [32].

#### 7. Nanocoatings

Nanocoatings are one of the most advanced technologies for surface modification of titanium alloys. These coatings consist of nanometer-thin layers that significantly improve the tribological properties of the material. Nanocoatings may include materials such as diamond nanoparticles or carbon nanotubes, which reduce the friction coefficient and increase wear resistance [33-34]. In biomedical applications, nanocoatings are particularly useful for implants and prostheses, where they improve biocompatibility and promote better integration with bone tissue [35]. The application of nanocoatings is a growing

area of research, offering new possibilities for improving the performance of titanium alloys in demanding environments [33-36].

### 3. CONCLUSION

Titanium alloys Ti-6Al-4V and Ti-6Al-7Nb are widely used in industrial and biomedical applications due to their excellent mechanical properties and good corrosion resistance. However, their poor friction and wear resistance present a challenge, especially in contact with other metals. The Ti-6Al-4V alloy is prone to intense galling, necessitating the use of specific surface modification, such as nitriding, to improve its wear resistance. Ti-6Al-7Nb, on the other hand, offers better biocompatibility and a lower coefficient of friction, making it a preferred choice for implants and biomedical devices.

Surface modification of these alloys is crucial for enhancing their performance properties. These methods provide better corrosion and wear resistance, making them a preferred choice for applications requiring durability and reliability. Advances in surface modification technologies for titanium and titanium alloys will continue to be a key factor in their broader use across various industrial and medical fields, ensuring high wear and corrosion resistance in extreme conditions.

### REFERENCES

- [1] Marin E., Lanzutti A., Biomedical Applications of Titanium Alloys: A Comprehensive Review, *Materials*, vol. 17, no. 1, p. 114, Dec. 2023, doi: 10.3390/ma17010114
- [2] Zhang et al., A new  $\alpha+\beta$  Ti-alloy with refined microstructures and enhanced mechanical properties in the as-cast state, *Scrip Mater* 207 (2022) 114260, doi: 10.1016/j.scriptamat.2021.114260.
- [3] Aniolek K., Barylski A., Kowalewski P., Kaptacz S., Investigation of Dry Sliding Friction, Wear and Mechanical Behavior of the Ti-6Al-7Nb Alloy after Thermal Oxidation, *Materials* 15 (9) (2022) 3168, doi: 10.3390/ma15093168
- [4] Kaur M., Singh K., Review on titanium and titanium based alloys as biomaterials for orthopaedic applications, *Materials Science and Engineering: C* 102 (2019) 844–862, doi: 10.1016/j.msec.2019.04.064
- [5] Bower K., Murray S., Reinhart A., Nieto A., Corrosion resistance of selective laser melted Ti-6Al-4V alloy in salt fog environment, *Results in Materials*, 8 (2020) 100122, doi: 10.1016/j.rinma.2020.100122
- [6] Pelleg J., Testing: Comparison of AM data with traditionally fabricated, Additive and Traditionally Manufactured Components, Elsevier (2020) 49–176, doi: 10.1016/B978-0-12-821918-8.00003-6
- [7] X. Zhou et al., Mechanical properties, corrosion behavior and cytotoxicity of Ti-6Al-4V alloy fabricated by laser metal deposition, *Mater Charact*, 179 (2021) 111302, doi: 10.1016/j.matchar.2021.111302
- [8] Avelar-Batista Wilson J.C., Banfield S., Housden J., Olivero C., Chapon P., On the response of Ti-6Al-4V and Ti-6Al-7Nb alloys to a Nitron-100 treatment, *Surf Coat Technol*, 260 (2014) 335–346, doi: 10.1016/j.surfcoat.2014.11.034
- [9] Hulka I., Florido-Suarez N.R., Mirza-Rosca J.C., Saceleanu A., Mechanical Properties and Corrosion Behavior of Thermally Treated Ti-6Al-7Nb Dental Alloy, *Materials*, 15 (11) (2022) 3813, doi: 10.3390/ma15113813
- [10] Zhang L.C., Chen L.Y., Wang L., Surface Modification of Titanium and Titanium Alloys: Technologies, Developments, and Future Interests, *Adv Eng Mater* 22 (5) (2020), doi: 10.1002/adem.201901258

- [11] X. Han et al., Surface modification techniques of titanium and titanium alloys for biomedical orthopaedics applications: A review, *Colloids Surf B Biointerfaces* 227 (2023) 113339, doi: 10.1016/j.colsurfb.2023.113339
- [12] T. Xue et al., Surface Modification Techniques of Titanium and its Alloys to Functionally Optimize Their Biomedical Properties: Thematic Review, *Front Bioeng Biotechnol*, 8 (2020), doi: 10.3389/fbioe.2020.603072
- [13] X. PAN et al., Investigations on femtosecond laser-induced surface modification and periodic micropatterning with anti-friction properties on Ti6Al4V titanium alloy, *Chinese Journal of Aeronautics* 35 (4) (2022) 521–537, doi: 10.1016/j.cja.2021.01.003
- [14] Pushp P., Dasharath S.M., Arati C., Classification and applications of titanium and its alloys, *Mater Today Proc*, 54 (2022) 537–542, doi: 10.1016/j.matpr.2022.01.008
- [15] Najafizadeh et al., Classification and applications of titanium and its alloys: A review, *Journal of Alloys and Compounds Communications* 3 (2024) 100019, doi: 10.1016/j.jacomc.2024.100019
- [16] Elias C.N., Lima J.H.C., Valiev R., Meyers M.A., Biomedical applications of titanium and its alloys, *JOM* 60 (3) (2008) 46–49, doi: 10.1007/s11837-008-0031-1
- [17] Long M., Rack H.J., Friction and surface behavior of selected titanium alloys during reciprocating-sliding motion, *Wear* 249 (1–2) (2001) 157–167, doi: 10.1016/S0043-1648(01)00517-8
- [18] Segu D.Z., Wang L.L., Hwang P., Kang S.W., Experimental characterization of friction and wear behavior of textured Titanium alloy (Ti-6Al-4V) for enhanced tribological performance, *Mater Res Express* 8 (8) (2021) 085008, doi: 10.1088/2053-1591/ac1ae6
- [19] Gupta et al., Tribological and surface morphological characteristics of titanium alloys: a review, *Archives of Civil and Mechanical Engineering* 22 (2) (2022) 72, doi: 10.1007/s43452-022-00392-x
- [20] Makurat-Kasprolewicz B., Ossowska A., Recent advances in electrochemically surface treated titanium and its alloys for biomedical applications: A review of anodic and plasma electrolytic oxidation methods, *Mater Today Commun*, 34 (2023) 105425, doi: 10.1016/j.mtcomm.2023.105425
- [21] Zhang L. Chen L., A Review on Biomedical Titanium Alloys: Recent Progress and Prospect, *Adv Eng Mater*, 21 (4) (2019), doi: 10.1002/adem.201801215
- [22] Echeverry-Rendón M., Galvis O., Aguirre R., Robledo S., Castaño J.G., Echeverría F., Modification of titanium alloys surface properties by plasma electrolytic oxidation (PEO) and influence on biological response, *J Mater Sci Mater Med*, 28 (11) (2017) 169, doi: 10.1007/s10856-017-5972-x
- [23] Dutta Majumdar J., Manna I., Laser surface engineering of titanium and its alloys for improved wear, corrosion and high-temperature oxidation resistance, *Laser Surface Engineering*, Elsevier (2015) 483–521, doi: 10.1016/B978-1-78242-074-3.00021-0
- [24] Zhao Y., Lu M., Fan Z., Huang S., Huang H., Laser deposition of wear-resistant titanium oxynitride/titanium composite coatings on Ti-6Al-4V alloy, *Appl Surf Sci* 531 (2020) 147212, doi: 10.1016/j.apsusc.2020.147212
- [25] Askari et al., Synthesis and characterization of nanocrystalline CVD diamond film on pure titanium using Ar/CH<sub>4</sub>/H<sub>2</sub> gas mixture, *Mater Lett* 61 (11–12) (2007) 2139–2142
- [26] Ranjan S., Mukherjee B., Islam A., Pandey K.K., Gupta R., Keshri A.K., Microstructure, mechanical and high temperature tribological behaviour of graphene nanoplatelets reinforced plasma sprayed titanium nitride coating, *J Eur Ceram Soc*, 40 (3) (2020) 660–671
- [27] Mendoza C., Gonzalez Z., Gordo E., Ferrari B., Castro Y., Protective nature of nano-TiN coatings shaped by EPD on Ti substrates, *J Eur Ceram Soc* 38 (2) (2018) 495–500
- [28] Rautray T.R., Narayanan R., Kim K.H., Ion implantation of titanium based biomaterials, *Prog Mater Sci* 56 (8) (2011) 1137–1177
- [29] Rautray T.R., Narayanan R., Kwon T., Kim K., Surface modification of titanium and titanium alloys by ion implantation, *J Biomed Mater Res B Appl Biomater* 93B (2) (2010) 581–591
- [30] Zhang X., Zhou W., Xi W., Advancements in incorporating metal ions onto the surface of biomedical titanium and its alloys via micro-arc oxidation: a research review, *Front Chem* 12 (2024)
- [31] Chouirfa H., Bouloussa H., Migonney V., Falentin-Daudré C., Review of titanium surface modification techniques and coatings for antibacterial applications, *Acta Biomater* 83 (2019) 37–54
- [32] C.-S. Chen et al., Improving the in vitro cell differentiation and in vivo osseointegration of titanium dental implant through oxygen plasma immersion ion implantation treatment, *Surf Coat Technol* 399 (2020) 126125
- [33] Mediaswanti K., Wen C., Berndt C.C., Wang J., Sputtered Hydroxyapatite Nanocoatings on Novel Titanium Alloys for Biomedical Applications, *Titanium Alloys - Advances in Properties Control*, InTech (2013)
- [34] S. Chen et al., Fabrication of superhydrophobic TA2 titanium alloy and preliminary assessment of its antifouling, self-cleaning, anti-icing, friction resistance, and corrosion resistance performance, *J Coat Technol Res* 21 (4) (2024) 1373–1383
- [35] Eliaz N., Corrosion of Metallic Biomaterials: A Review, *Materials* 12 (3) (2019) 407
- [36] Takahashi K., Mori K., Takebe H., Application of Titanium and its Alloys for Automobile Parts, *MATEC Web of Conferences* 321 (2020) 02003