

Review

Influence of Laser Modification on the Surface Character of Biomaterials: Titanium and Its Alloys—A Review

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Abstract: Laser surface modification is a widely available and simple technique that can be applied to different types of materials. It has been shown that by using a laser heat source, reproducible surfaces can be obtained, which is particularly important when developing materials for medical applications. The laser modification of titanium and its alloys is advantageous due to the possibility of controlling selected parameters and properties of the material, which offers the prospect of obtaining a material with the characteristics required for biomedical applications. This paper analyzes the effect of laser modification without material growth on titanium and its alloys. It addresses issues related to the surface roughness parameters, wettability, and corrosion resistance, and discusses how laser modification changes the hardness and wear resistance of materials. A thorough review of the literature on the subject provides a basis for the scientific community to develop further experiments based on the already investigated relationships between the effects of the laser beam and the surface at the macro, micro, and nano level.

Keywords: laser modification; titanium; titanium alloys

Citation: Sypniewska, J.; Szkodo, M. Influence of Laser Modification on the Surface Character of Biomaterials: Titanium and Its Alloys—A Review. *Coatings* **2022**, *12*, 1371. <https://doi.org/10.3390/coatings12101371>

Academic Editor: Matic Jovičević-Klug

Received: 21 August 2022
Accepted: 8 September 2022
Published: 20 September 2022

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1. Introduction

Surface modifications of materials provide the base for achieving specific material properties for specific applications. The main advantage of laser surface modification is the ability to improve the properties of different materials [1,2]. In addition, the precision, elasticity, the possibility of parameters control, and the repeatability of this process are indicated as an advantage, as is the small heat-affected zone resulting from the modification [3,4]. Because of the high degree of process sophistication, it is also possible to carry out the process without direct human intervention, thus reducing the risk of negative effects on the body [5].

Researchers mainly use lasers such as a femtosecond laser [6], Nd: YAG laser [7–10], CO₂ laser [11], diode [12,13], and fiber laser [14]. Firstly, they provide the possibility to carry out modification processes by adding a coating of the same or another material. Moreover, they are used for modifications with no further addition of materials [1]. Figure 1 presents a classification of laser machining based on an increase or no increase in material. This article is primarily concerned with laser remelting and texturing, as these two techniques are the most commonly used in the modification of biomaterials. Laser remelting is a technique based on remelting the surface of a material to change its morphology and structure without a specific modification objective, to generally improve the properties affected by a laser beam or, for example, when there is talk of modifying the density of the material or the hardness [7,15–17]. Laser texturing involves melting the material and then cooling it to produce a specific pattern on the surface of the material [18]. A combination of laser hardening and laser texturing is also found in the literature [19]. Laser hardening is a technique aimed at improving the hardness of materials using a laser beam. Furthermore, it has the advantage of being able to increase the wear resistance and

improve fatigue properties. [20] Surface modification with no addition of a material, which will be discussed in the following work, directly affects a change in wettability and roughness, corrosion resistance, hardness of the material, and wear resistance. Laser modification is closely related to a change in the surface microstructure and influences the roughness and wettability of materials [21–24]. The advantages of using lasers to modify biomedical materials are the ability to control the effect of heat on the surface structure of the materials due to the local action of a laser pulse on the surface, the small heat-affected zone, and the fact that the process is clean and does not cause material loss [25,26].

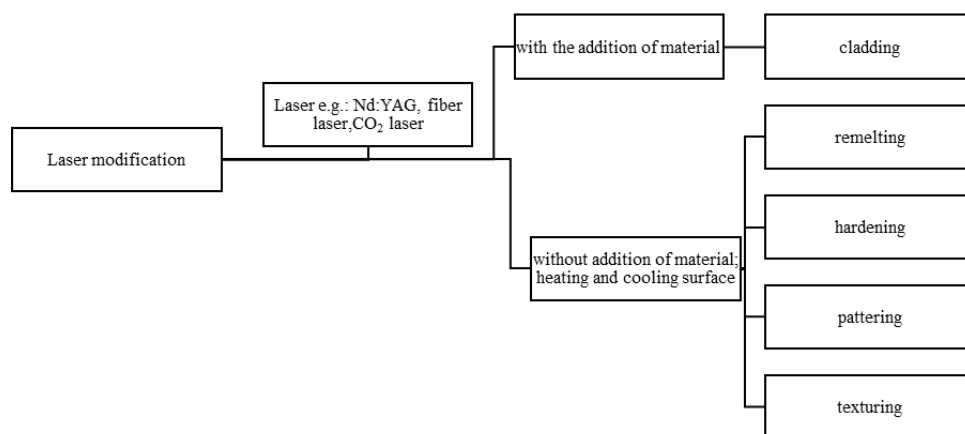


Figure 1. Graphic interpretation of laser modification possibilities based on [1,13,20–22].

The process of the heat treatment of materials by laser is mainly related to the treatment of metallic materials such as aluminum, steel, and its alloys, as well as titanium [2,3,27,28]. Many research efforts are currently focused on gaining a thorough understanding of the properties of titanium and its alloys. Further, efforts are being made to improve these properties to produce a material dedicated to applications.

Titanium and its alloys are widely used in various industries due to their low density. This family of materials has its uses in the manufacture of parts for motorcycles, and sports vehicles to reduce their weight [29,30]. In the aerospace industry, these materials are the third group of materials, after nickel-based materials, in terms of their frequency of use, not only because of their low density, but mainly because of their resistance to corrosion and high temperatures (e.g., alpha alloys and α/β alloys) [31–33]. Considerable attention is given to this material when it comes to medical applications [34,35]. In applications in the field of dental implantology, titanium alloys are used for the production of dental crowns and bridges primarily due to the reduced risk in an allergic reaction and they have a beneficial effect on the process of osseointegration [36,37]. The use of titanium and its alloys is based on its high corrosion resistance, better than steel and cobalt–chromium alloys, owing to the properties of self-assimilation, which are beneficial due to the environment of the body in which the implants are placed [38–41]. In the case of titanium and its alloys, it is said to have little effect on the human body. Pure titanium is a biocompatible material, as are all of its alloys. The alloying elements used to produce titanium alloys, however, do pose a problem, but it should be noted, that titanium and its alloys have hemolytic indices below a value that would indicate the possibility of the formation of embolisms or clots as a result of the presence of this material in the body [42]. Studies by Chen et al. indicate that the presence of vanadium and aluminum in the human body leads to disorders of the nervous system, brain diseases, and circulatory diseases, while also affecting the softening of bone tissue; however, it is indicated that alloys containing



aluminum and vanadium ($\alpha + \beta$ alloys) have mechanical properties on the same level as β alloys. In implantology, aluminum–vanadium alloys are used primarily to produce fracture fixation plates, spinal column components, and connecting elements such as rods, wires, and screws [43]. Review papers over the years related to modifications using laser beams have reported on the benefits of modification for industrial applications (matrix-enhanced laser modification) [44], but they mainly confirm the benefits for biomedical applications [45,46]. Paper [45] focuses on the effect of laser surface texturing on the antimicrobial properties and biological activity of titanium, while a 2005 article [46] provides an overview of the possible types of surface modifications available for various biomaterials and discusses in detail laser modification in the context of the biocompatibility of the modified material. The present review focuses on the mechanical properties of the surface of titanium and its alloys after laser modification. Attention is paid to the properties directly related to the requirements for biomedical materials, such as an adequate material hardness, wear, corrosion resistance, and affinity of the modified surface to bone-forming cells.

A literature review on the effects of laser modification on titanium and its alloys was conducted to present the current state of the art in this field and to highlight the topicality of the problem of the laser modification of titanium and its alloys for biomedical applications due to the requirements that are placed on biomaterials.

2. Methods

This systematic review used the databases: ResearchGate, Science Direct, and Scopus. Google Scholar was also used to analyze the trends in the laser modification of titanium and its alloys. The searching strategy was based on the “laser modification”, “laser treatment”, “laser remelting”, “laser surface modification of titanium and its alloys”, and “modification of titanium and its alloys” terms. A bibliography of 175 literature references was collected and extracted from over 200 collected papers. Figure 2 shows the number of articles from each year. The literature review was based mainly on works from 2019 to 2022, which allowed us to discuss issues according to the current state of knowledge on the laser surface modification of titanium and its alloys for selected parameters and properties. The paper discusses the effect of the laser treatment of titanium and its alloys on the surface roughness and wettability, corrosion resistance, and hardness with the indications of micro and macro hardness and wear resistance.

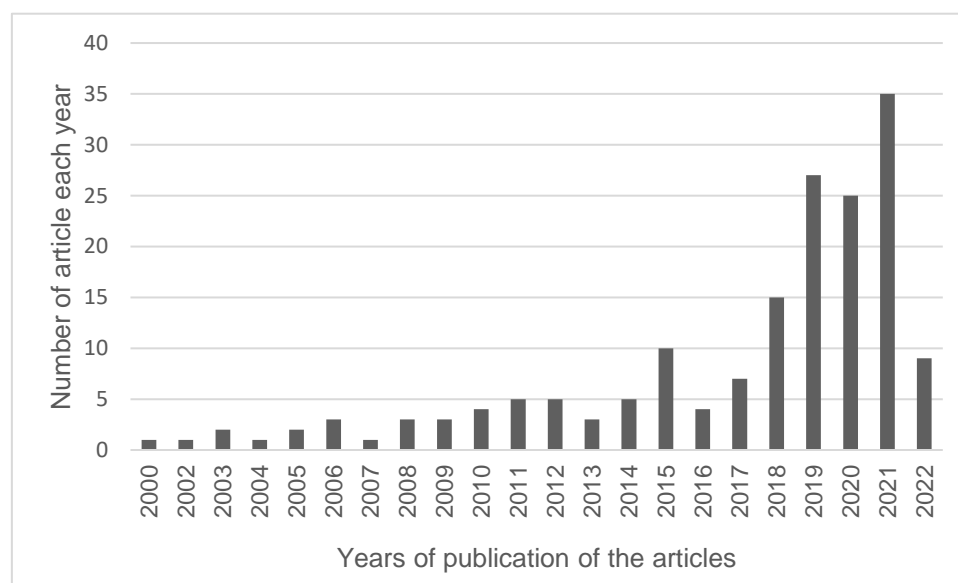


Figure 2. Distribution of the number of articles used per year.

3. Roughness and Wettability

Roughness and surface wettability are very often compared by authors to determine the relationship between these properties [47,48]. The study of these parameters in the case of titanium modifications is very important due to the use of titanium in biomedicine. The evaluation of the roughness parameter is important because an increase in this index has a positive effect on the cell adhesion during osseointegration and on the connection between the bone and an implant [49]. The use of titanium and its alloys in biomedicine is indicated for the manufacture of artificial hip joints, artificial knee joints, bone plates, fracture fixation screws, prosthetic heart valves, pacemakers, and the production of artificial hearts [50,51]. Depending on the area of aspiration of titanium and its alloys, a different surface roughness is required of a biomaterial. For example, heart valve implants, the artificial heart, and other components of the circulatory system must be made of a medium to low-roughness titanium to avoid the formation of areas where blood cells could agglomerate and form blockages, thus stopping the blood flow [52]. In addition, titanium itself possesses anti-thrombogenic properties, and for implant applications, it is necessary to improve the properties of the structure. In the case of osseous dental implants, it is said that components with a high degree of surface roughness are necessary due to the osseointegration process that occurs. An increase in the surface roughness is associated with an increase in the growth surface of osteoblasts and protein polyfusion [53]. Menci et al. [24] point out that laser modification with different types of lasers (e.g., a fiber laser or Nd: YAG laser) is necessary, as the hip implants in question are composed of several elements and each part must have different surface properties. The acetabulum and femoral stem need to be rougher to stimulate bone osseointegration, while the femoral head and distal part of the femoral stem need to be smoother to minimize wear.

In paper [49] it was shown that the roughness of the pore walls created by laser modification was characterized by the roughness parameters, S_a and S_q , with a higher value than on the inter-pore surfaces. The values of S_a and S_q for the inter-pore surfaces were $0.029 \mu\text{m}$ and $0.04 \mu\text{m}$, respectively, while those for the pore walls were 0.126 and $0.149 \mu\text{m}$, respectively. The authors concluded from their studies on bone deposition that a higher pore roughness improves the migration of bone-forming cells and also increases the possible surface area for osteoblast attachment to the implant. Furthermore, a high surface roughness is desirable due to increased biointegration and a decreased risk of implant rejection in the body [8].

In papers [8,54–60], an Nd: YAG laser was used to modify titanium alloys and pure titanium. In Table 1, the Nd: YAG laser operating parameters are presented for the literature reviewed subject. In the study, the Nd: YAG laser modification was performed for different laser operating parameters. The effects of varying laser operating parameters on the surface roughness and wettability, which are directly related to the phenomenon of bone cell adhesion, were investigated in a study from 2013, where Györgyey et al. showed [58] a decrease in the R_a roughness parameters using a frequency-doubled Q-switched Nd: YAG laser and a KrF excimer laser. In a 2020 editorial [8] it was observed that the modification of the titanium alloy Ti13Nb13Zr and pure titanium CP-Ti using an Nd: YAG laser caused an increase in the surface roughness. In addition, it was shown that the higher the laser power, the higher the roughness parameters. Additionally, in research work [8] it was pointed out that titanium alloys were rougher than pure titanium before and after laser treatment. Research of [57,61–63] also confirmed that laser modification, regardless of the type of laser, along with increasing the laser parameters, increased the roughness. In paper [57] it was shown that laser processing increased the roughness parameters by approximately 2.8 to 7.5 times at different frequencies relative to the native material. AFM surface texture tests at 10 Hz and 7 Hz successively yielded R_a parameters of 394.35 nm and 279.53 nm, respectively, while this parameter for the reference sample of the Ti6Al4V titanium alloy was 127.20 nm [57].

Table 1. Parameters of Nd: YAG laser modification to improve the roughness of titanium and its alloys.

Laser	Material	Environment	Laser Output Energy	Voltage	Laser Pulse Duration	Irradiation Time	Scanning Speed	Frequency	Average Expansive Area	Fluency/Power	Shot of Pulses	Roughness Parameters	Reference
Nd: YAG	Ti13Nb13Zr and CP-Ti	air/argon	5,30 mJ	-	150 ps	5s	-	10 Hz	-	-	50	(Table 2)	[8]
	Ti15Mo and cpTi grade 2	-	-	-	-	-	0–200 mm/s	20–35 Hz	14 mm ²	1.9 J/cm ³	-	-	[54]
	technically pure VT-1–00 titanium	Air	-	250–400 V	3–10 ms	-	-	1–5 Hz	-	-	1–5	R _a = 3.95 μm R _z = 21.2 μm R _{max} = 29.01 μm S _m = 91 μm	[55]
	Ti6Al4V	-	-	-	-	-	30 mm/min	-	-	200 W	-	R _a = 0.45 μm	[56]
	Ti6Al4V	Argon	-	-	7 ms	-	1 mm/s	1, 3, 5, 7, 10, 15, 20 Hz	-	average power 300 W; peak power 2.1 kW	-	R _a for 10 Hz z = 0.394 μm R _a for 7 Hz z = 0.127 R _a μm	
	CP4) Ti rods	Air	-	-	-	-	-	-	-	1–1.5 J/cm ³	200, 300, 400	-	[58]
	Ti6Al4V	Air	95 mJ	-	-	120 ns	-	10 Hz	-	0.95 W	-	-	[59]
	Ti45Nb	Air, argon, nitrogen	-	-	150 ps	5 ns; 15 s	-	10 Hz	7.1 × 10 ⁻⁴ cm ²	0.13–0.38 J/cm ²	50, 150	(Table 2)	[60]

Table 2. Surface roughness depended on the laser modification environment [8,60].

Sample [60]	Ti4Nb											
Laser modification environment	Argon				Air				Nitrogen			
Laser modifications parameters	5 mJ 50 pulses	5 mJ 150 pulses	15 mJ 150 pulses	15 mJ 150 pulses	5 mJ 50 pulses	5 mJ 150 pulses	15 mJ 150 pulses	15 mJ 150 pulses	5 mJ 50 pulses	5 mJ 150 pulses	15 mJ 150 pulses	15 mJ 150 pulses
Surface roughness [μm]	1.026	2.053	1.414	3.062	0.551	0.921	0.884	0.949	0.839	1.148	0.647	0.804
Sample [8]	Ti13Nb13Zr											
Laser modification environment	Air						Argon					
Laser modifications parameters	5 mJ 5 s			30 mJ 5 s			5 mJ 5 s			30 mJ 5 s		
Surface roughness [μm]	0.428			0.988			0.701			1.366		
Sample [8]	CP-Ti											
Laser modification environment	Air						Argon					
Laser modifications parameters	5 mJ 5 s			30 mJ 5 s			5 mJ 5 s			30 mJ 5 s		
Surface roughness [μm]	0.258			0.931			0.927			1.842		

The references state that the laser treatment of titanium surfaces allows for controlling the roughness parameters, R_a , R_z , and R_{max} , in a wide range [55]. The use of a modern fiber laser engraving method [64] allowed the achievement of a surface with a higher roughness than the Ti6Al4V native material. Meanwhile, comparing the results of the roughness measurements at different laser operating parameters, it was observed that with an increase in the laser operating parameters (e.g., groove distance and frequency), there was a decrease in the value of the roughness and an increase in the value of the wetting angle, which was associated with the determination of the surface of the samples as hydrophobic.

Studies [8,60,65] also indicate that the operating environment of the Nd: YAG laser affects the surface roughness and morphologies. The results of EDS [8] have shown that the presence of argon affects the reduction of oxygen molecules for both commercially pure titanium and Ti13Nb13Zr titanium alloy samples; however, the modification carried out in the presence of air caused a strong passivation of the coating and, thus, increased the amount of oxygen on the surface, while the surface roughness for the modified surfaces in the presence of air was lower. Conducting the modification in the presence of argon for each parameter variant results in the roughest surface (Table 2). The laser modification in a nitrogen environment for low power and number of pulses presented in work [60] showed a higher roughness than for the same modification in the presence of air, while in the case of a modification in the presence of argon the modified surfaces—for different laser powers of 5 mJ and 15 mJ and the number of pulses of 50 and 150—were characterized by the highest roughness among all the modified surfaces. The conclusions in [60] are confirmed in [65], where the reason for the lower surface roughness after modification in a nitrogen environment was due to the formation of titanium and nitrogen compounds and the formation of a smaller heat-affected zone. The authors of that article also indicated that for a smaller number of pulses performed, the surface roughness was lower.

Lawrence et al. [56] 2006, presented the idea that laser processing increases the roughness parameters and improves the surface wettability. In Table 3, the literature on the results of the influence of a laser treatment on the character of the surface wettability is summarized. Menci et al. [24] searched for a direct relationship between the contact angle and the Sa parameter for Ti11.5Mo6Zr4.5Sn titanium alloy samples modified by an Nd: YAG laser and fiber laser for different parameters. Wenzel's claim was referred to, which states that increasing the roughness parameter (r) increases the wettability of the surface (where θ_y is the contact angle of an ideal flat surface and θ_w is the contact angle of a rough surface) [66]:

$$\cos\theta_w = r\cos\theta_y$$

The realization of this equation in the work of [24] indicates hydrophilic surface properties because the initial properties of titanium were improved by changing the surface texture (increase in roughness) and there was an increase in droplet diffusion [67].

Table 3. Wettability results on titanium and its alloys observed in the article.

Surface Property	Author, Year, and Reference	Short Conclusion
Wettability	Hao et al., 2005 [68]	Observation and study of the surface of laser-modified Ti6Al4V alloy showed an increase in the surface wettability which is beneficial for medical applications of titanium alloys. The increase in the contact angle after laser modification is a result, according to the authors, of an increase in the surface energy of the modified material and an increase in roughness parameters.
	Lawrence et al., 2006 [56]	Lawrence et al. demonstrated that laser treatment improves the surface wettability as a result of a change in the surface energy, an increase in the oxygen content, and an increase in the surface roughness. The cell studies carried out revealed an increase in bone cell adhesion and proliferation for Ti6Al4V titanium alloy samples subjected to laser modification, compared to a titanium alloy without modification.

Cunha, A. et al., 2013 [69]	Obtaining an anisotropic surface by modification is beneficial for controlling the surface wettability and this property is also indicated to improve stem cell adhesion.
May et al., 2015 [70]	The surface anisotropy of titanium alloy Ti6Al4V subjected to fiber-laser system modification was demonstrated. Wetting angles were smaller for the measurement performed perpendicularly for each laser operating frequency. The formation of contact anisotropy after laser modification was related to the frequency of the laser work, and increasing this parameter decreased the anisotropy.
Raimbault O. et al., 2016 [71]	The paper focused on the bioactivity of cells towards a femtosecond laser-modified surface but also examined the wettability of the Ti6Al4V titanium alloy, which was determined by measuring the contact angle. It was shown that the storage medium had a great influence on the change of the wettability characteristics of the modified samples. Samples stored in boiling water were slower to change their character to hydrophobic ones due to the slowing down of the passivation process, and the atmospheric environment accelerated these changes.
Rotella 2017 [72]	The authors used three methods for the surface modification of titanium alloy Ti6Al4V, one of them was a femtosecond laser treatment. The hydrophobic character of the laser-modified samples was observed, but at the same time, it was pointed out that this was not a disadvantage of such a surface because it gives, in a long-term context, a chance for a stronger bonding of the cells with the laser-modified implant.
Lu et al., 2018 [73]	A laser treatment at different laser fluence values was applied to pure titanium samples and then they were chemically treated. For each of the modification combinations, it was shown that the femtosecond laser modifications decreased the contact angle immediately after the laser treatment, while the contact angle increased after the modification. The possibility to obtain a stable structure with hydrophobic properties was pointed out in the paper as the most important advantage of such a modification.
Pires et al., 2017 [54]	The Nd: YAG laser treatment produced a superhydrophilic surface. The laser-modified surface consisted of more oxygen, which was one of the factors influencing the change in surface wettability. It was indicated that the use of this type of laser allows for the control of parameters important for bone cells.
Menci et al., 2019 [24]	In this study, a laser beam modification was performed using two different types of Nd: YAG laser and fiber laser, for different laser wavelengths. It was shown that a fiber laser processing ns 1064 nm produces the highest surface roughness with the greatest reduction in wetting angle. The paper also presents the possibility of using individual lasers with specific parameters to process specific implant components because of the roughness that can be achieved with them.
Murillo et al., 2019 [74]	It was observed that immediately after the modification of a Ti6Al4V titanium alloy with a UV ns laser and IR-fs pulsed lasers, the surface exhibited hydrophilic properties. In this study, the effect of the sample holding environment of titanium on material aging was investigated.
Shaikh et al., 2019 [75]	In this study, a decrease in the contact angle was observed for Ti6Al4V titanium alloy samples which underwent laser modification. It was also observed that the surface of the samples after laser treatment became hydrophilic immediately after the modification; however, during the storage of the material, the contact angle was tested again, and the results showed a change in the surface character toward a hydrophobic one. The authors suggested that this could be due to the oxidation of the modified film as well as contaminants deposited on the sample (the samples were stored in an atmospheric environment).
Dou et al., 2020 [76]	An increase in hydrophilicity with an increasing laser fluence was observed. The surface hydrophilicity was not stable, and the wettability of the surface changed to hydrophobic properties with time. The need for research on the stability of surface hydrophilicity was indicated.
Wang et al., 2021 [77]	A 355 nm UV laser modification of commercially pure titanium was carried out. In this study, the possibility of controlling the wettability by light and sample heating was demonstrated. The samples showed a superhydrophilic surface immediately after laser modification.
Mukherjee et al., 2021 [78]	In this paper, the laser modification of titanium alloy Ti6Al4V using a Yb-doped fiber laser was carried out. It was shown that the surface produced by the laser was anisotropic, which revealed that the contact angle for water was different for a parallel and perpendicular incidence of a drop on the surface. It was shown that in the direction parallel to the laser beam direction, the wetting of the surface was higher as a result of droplet propagation along the corrugation grooves.
Wang et al., 2021 [79]	A Ti6Al4V titanium alloy was modified with a UV laser at a wavelength of 355 nm. The results of the contact angle measurements were presented for three conditions: for the untreated sample (hydrophilic surface), the sample after laser treatment (superhydrophilic surface), and the sample

	modified with a laser and additionally subjected to a heat treatment (hydrophobic surface). For the same samples, an erosion test was performed and it was observed that the fastest erosion process occurred for the laser-modified samples and the slowest for those with a hydrophobic surface.
Singh et al., 2021 [80]	In this study, a CO ₂ laser modification was carried out on titanium Ti6Al4V alloys. After the modification, the values of the contact angle and surface energy were investigated. It was found that for the laser-modified surface, the contact angle was higher than for the unmodified samples, and the surface energy also increased. It was also found that a decrease in the surface energy resulted in a decrease in the affinity of the modified surface for bacteria, which is beneficial for the potential use of the material in implant production.
Li et al., 2022 [81]	Pure titanium samples were subjected to laser surface texturing. Wetting angle studies were carried out using distilled water and modified-simulated body fluid (m-SBF). For both fluids, the laser-modified surface showed an increased wettability. It was indicated that the drops on the structure with a higher roughness realized Wenzel's law, which explained the decrease in the contact angle. The wetting angle for the water was higher than for the m-SBF, which gave information that cells would grow better on such a substrate.

The literature identifies four terms for surface wettability: superhydrophilic, hydrophilic, hydrophobic, and superhydrophobic, concerning a drop of water falling on a surface Figure 3 [59].

The researchers, Lawrence et al. [56], Menci et al. [24] and Pries et al. [54], treated titanium alloys successively with an Nd: YAG and Yd: YAG laser, and based on contact angle studies, they showed that a laser modification increases the wettability of the sample surface successively for fluids such as human blood, human blood plasma, glycerol and 4-acetanol [56] and water [24]. A decrease in the wetting angle is also shown in Figure 4 for the modification made with the Nd: YAG laser [82]. Pries et al. [54] revealed that the contact angle measured after a laser treatment was 0°. Singh et al. [80] on the other hand, observed that the laser modification of a titanium alloy resulted in a decreased surface roughness, resulting in coatings with a lower wettability than unmodified samples.

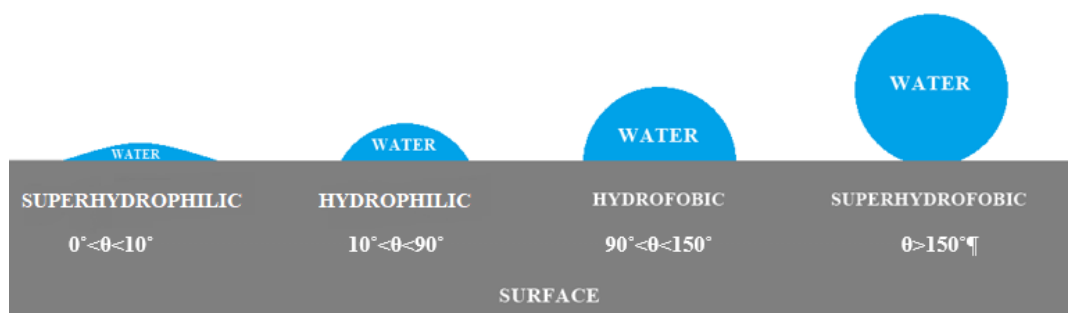


Figure 3. Categories of wettability based on [59,66].

Researchers Lawrence et al. [56] Menci et al. [24] and Pries et al. [54] treated titanium alloys successively with Nd: YAG and Yd: YAG laser, based on contact angle studies they showed that the laser modification increases the wettability of the sample surface successively for fluids such as human blood, human blood plasma, glycerol and 4-acetanol [56] and water [24]. The decrease in wetting angle is also shown in figure 4 for the modification made with the Nd:YAG laser [82]. Pries et al. [54] revealed that the contact angle measured after laser treatment is 0°. Singh et al. [80] on the other hand, observed that laser modification of titanium alloy resulted in decreased surface roughness resulting in coatings with lower wettability than unmodified samples.

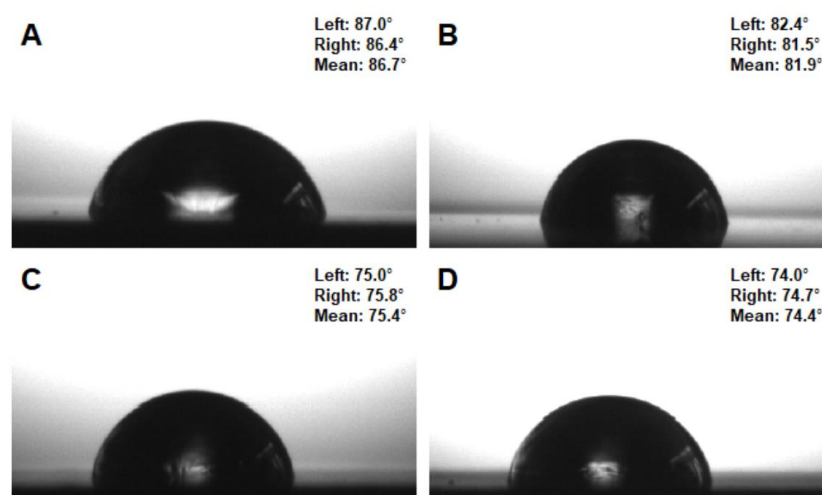


Figure 4. Wettability of material for (A) base material Ti13Nb13Zr, (B) laser modified sample 700 W, (C) laser modified sample 1000 W, and (D) laser modified sample 700 + 1000 W [82].

Conversely, in paper [76], a Ti: sapphire chirped-pulse regenerative amplification laser system with a central wavelength of 800 nm, was used to modify a Ti4Al6V alloy. Initially, the investigated surfaces were characterized by the hydrophilic nature of the modified surface. In the experiment, the contact angle measurements were performed cyclically for up to 155 days after the modification. The observations showed that the effect of the modified surfaces changed from hydrophilic to hydrophobic. Analogous results were also reported in the work of [69,74,75,81,83] for the contact angle for water and for Hank's balanced salt solution (HBSS) for titanium and titanium alloys.

In the research of [73], an alloy was laser-treated with a femtosecond laser, followed by an additional hydrothermal treatment and oxidation. The application of extra modifications did not change the previously established theory that states that with time, the contact angle of laser-modified surfaces increases. Raimbault et al. [71] pointed out that the increase in the contact angle after a certain time after a laser treatment increases due to the increasing passivation of the surface. Moreover, this paper shows that the environment of repository-modified samples is important due to the changing character of the sample wetting. Keeping the laser-modified TA6V samples in an air environment was associated with a faster change in the surface character from hydrophilic to hydrophobic, while an increase in the wetting angle for samples stored in boiling water was smaller. In the study of [72], it is depicted that the change in surface wettability from hydrophilic to hydrophobic after a laser treatment does not adversely affect cell adhesion to the material. A better way to illustrate the bonding of a surface to a water droplet is to use the Cassie Baxter model, which takes into account the idea that the contact between a droplet and a surface is affected by air trapped in the irregularities [84]; therefore, an increase in the wetting angle is not uniquely associated with a weakening of the bond between the material and the cells. In addition, the bond is also affected by mechanical stress, which is related to the amount of cracking on the material surface [72].

The references of [62,74,82,83] indicate that laser-modified surfaces can exhibit anisotropic as well as isotropic properties depending on the laser operating parameters [69]. The anisotropy of a surface is more favorable due to its higher wettability than for isotropic surfaces and the contact angles for anisotropic surfaces will be different for parallel and perpendicular directions [70,78,85]. Surface modification resulting in an anisotropic surface is very important for the ability to control the wettability of materials [69], and in addition, due to the medical use of titanium and its alloys, the development of an anisotropic surface is beneficial because of improved osseointegration conditions [47]. It is indicated that the wettability character of laser-modified surfaces can be controlled and

changed by external factors such as heat [77,79]. In the study of [77], the hydrophilic properties of a titanium alloy surface were observed immediately after laser modification. It was shown that it was possible to manipulate the character of the surface wettability by using the heating of the samples and UV radiation, which allowed the reversible transformation of the surface from hydrophilic to hydrophobic and the other way around.

4. Corrosion

Titanium and its alloys are characterized by a very high chemical activity. The Pourbaix diagram shows that titanium is a metal that passivates very quickly [86]. The natural, very good corrosion resistance of titanium and its alloys is indicated [87–91]. Additionally, the corrosion behavior is influenced by the presence of β -stabilizing alloying elements and their role in the stability and thickness of the passive layer formed [92]. An important direction of research is the study of the corrosion resistance of titanium bio-alloys [93,94], and to improve this property, it is necessary to limit as far as possible the release of metal ions into the body, since the possibility of adverse health effects due to the presence of, e.g., V or Al in the body has been identified [42,95,96].

It has been shown that titanium and its alloys are stable materials when exposed to environments that react with their surface, but the problem that arises in the root cause of this material is the development of fatigue corrosion, which occurs as a result of the loads on implants. For example, the stress-shielding effect that occurs in implants is due to the greater hardness of titanium than bone. The literature also states that cyclic loads induced by walking affect the corrosion resistance of titanium materials. Moreover, alloying additives in titanium alloys can have negative effects such as vanadium, aluminum, or chromium, whereas alloys with a density of, for example, niobium or tantalum lead to the formation of oxide layers which improve the root resistance of titanium alloys [97].

Laser modification allows the free manipulation of the surface roughness and wettability, which has a significant impact on the corrosion resistance of a material [98,99]. In 2012 [100], corrosion tests on pure titanium and titanium alloy with aluminum and vanadium were performed and based on the corrosion intensity (IA/cm^2), and it was observed that there was a decrease in the corrosion and corrosion-fatigue behavior of the studied materials after laser modification. It was indicated that the reason for the decrease in the corrosion resistance was the presence of residual stresses and small grain sizes in the modified surface, and the resulting microstructure changes differed in potential. The literature indicates that the grain size is affected by the modification of heat [101].

In contrast, the work of [102] cites results from 1984 (Picraux and Pope), 2000 (Suzuki et al.), and 2002 (Yue et al.), which state that laser modification improves the corrosion resistance in, for example, Hank's solution. Travessa et al. [103] showed that laser modification caused significant metallurgical and chemical changes on the surface of an alloy, including the formation of oxides, which resulted in a significant improvement of the corrosion properties compared to metal not subjected to laser treatment. It was also observed, among other things, in the potentiodynamic polarization curves. Navarro [26] showed that a femtosecond laser modification caused changes in the surface of modified samples with different porosities, resulting in an increased impedance (Figure 5). Tests carried out by [103,104] indicated that a thicker oxide or nitride layer formed after laser modification on a material surface, improved the corrosion resistance of a titanium alloy. It was observed that the surface structure after the laser modification, when there were unevenly distributed phase components in it, affected the weakening of the corrosion resistance of the material. The corrosion resistance test carried out in a Ringer's solution Ti6Al4V titanium alloy [105,106], showed an increase in the corrosion resistance in acidic media. Whereas in the papers of [107,108], an increased corrosion resistance of laser-modified samples in Hank's solution and saline solution was shown.

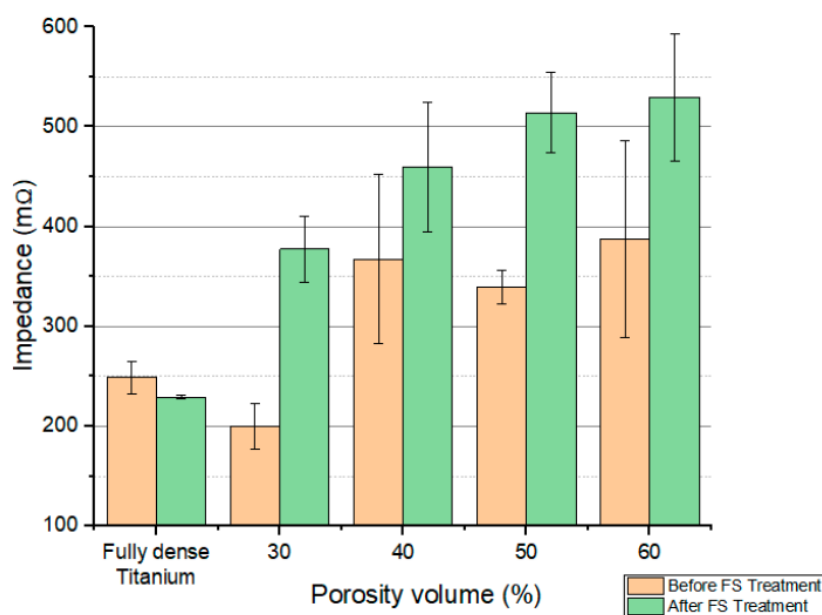


Figure 5. The change of impedance after laser modification for samples with different porosity volume [26].

Researchers in [78,109,110] investigated the effect of laser remelting on pitting and electrochemical corrosion resistance. An analysis of the polarization curves in the work [109] showed an increased resistance to pitting corrosion, which according to the authors was due to a microstructural modification caused by the rapid solidification that occurred during the laser remelting of the surface. Dhara et al. [78] have shown, based on obtained polarization curves, that as a result of the modification, the passive film formed a stable barrier against corrosion. In the paper of [106] it was pointed out that a higher electrochemical resistance was due to the reduction in the volume of the α and β phase, and the thickening of the surface texture. SEM and AFM studies carried out in [108] indicated that the laser modification formed a more reproducible and smoother topography, which increased the corrosion resistance of the material, and a stabilization of the passive layer on the titanium surface was observed, making it less susceptible to further growth [111]. Tests carried out on the chemical composition of the material showed an increase in the presence of nitrides, which acted as a barrier to the ingress of other molecules, and which was considered a condition that could improve the corrosion resistance of a material. An improvement in corrosion resistance by laser ablation was undertaken by [112] in their work, in which they removed the oxide layer, which gave their material a low corrosion resistance, and via the laser ablation, produced a corrosion-resistant oxide layer. This could be observed from an increase in the self-corrosion potential for different energy doses and a decrease in the self-corrosion current, which numerically reflected the corrosion rate of the material; therefore, indicating that the lower the surface corrosion rate the better the corrosion resistance.

5. Hardness

The hardness of titanium and its alloys is reported in the literature to be higher than the hardness of steel on the Vickers scale [113]. For example, titanium alloy Ti6Al4V has a hardness of HV higher (340 HV) than pure titanium (200 HV), which is related to the presence of alloying elements [114,115]. The surface modifications of these materials aim to improve the hardness and mechanical parameters to increase the residence time of an implant in the body [116]. The hardness of the materials used for implants is important because an increase in the material hardness is associated with an increase in the wear resistance [116]. The literature also indicates that the high hardness of a material can

adversely affect the behavior of the biomaterial in the body [117]. Laser modification, on the other hand, allows a controlled change in the parameters. Hardness, for example, is widely discussed in the field of orthopedic implants, such as hip and knee implants, because of the need to control the shielding effect of the implant in the bone, and the importance of this parameter, as orthopedic implants are placed under a certain pressure in the body, meaning that the implant must counterbalance this pressure to perform its function properly [118].

A systematic review [119] and research by the authors [10,105,120–122] on the various techniques of the surface modification of titanium have observed an increase in the hardness of materials as a result of laser modification, which has its theoretical basis in [123], where it was indicated that by using a heat source it was possible to control changes in the hardness of materials. Table 4 shows the hardness values obtained for modified titanium alloys and pure titanium using different laser types and parameters. In Figure 6 it is also shown that laser modification improved the nano-hardness of Ti13Nb13Zr alloy samples after a laser modification by an Nd: YAG laser.

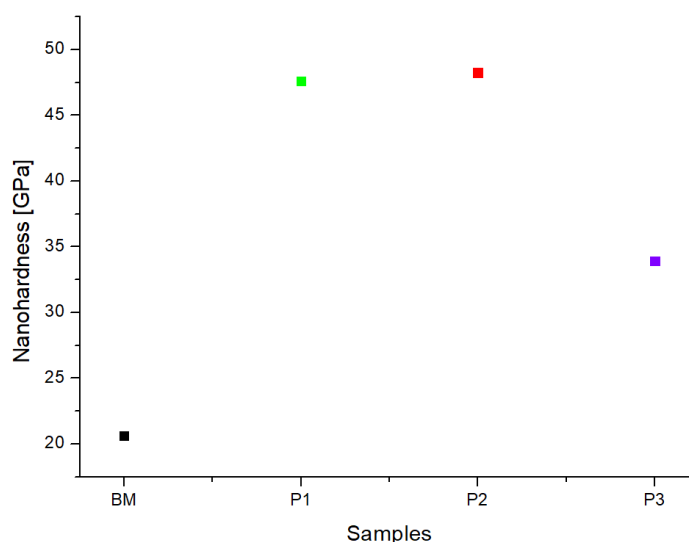


Figure 6. Nano-hardness of laser modified samples. BM: base material, P1: laser modified sample with 800 W and scan rate 60%, P2: laser modified sample with 800 W and scan rate 30%, P3: laser modified sample with 900 W and scan rate 60% [82].

In paper [105], the difference in the hardness value HV between the remelted material and the base material was about 300 HV. The study on the hardness of a titanium alloy was carried out by Khorram et al. [124] which indicated an increase in hardness of 36%. Additionally, Zhang et al. [125] indicated an increase in hardness after laser modification of 60%, while Ushakov et al. [126] determined that the possibility of increasing the Vickers hardness after a laser treatment ranged between 20% and 40%. Moreover, the increase in microhardness was accompanied by an increase in the fracture toughness. The laser modification of porous titanium in the research of [127] resulted in an increase in the hardness at the pore pillars, while an increase in the pore size in the titanium sample resulted in a decrease in the hardness. A significant effect of the pore size on the surface hardening potential by a laser modification was demonstrated.

The change in hardness of samples after laser remelting varies due to the phase transformations occurring during the cooling process [24,109,110]. The increase in material hardness is due to the transformation of the β -phase at high temperatures from about 900 °C to 1050 °C [128], into the α phase and the martensitic α phase, which is hard but very brittle [121,129–131], and the creation of the ω -phase [132,133]. After a laser-induced heat treatment, the formation of a martensitic α -phase was observed as a result of the

transformation of the alpha-phase of titanium alloys initially into a beta-phase, and then during the rapid cooling of a material after laser treatment, a martensitic α -phase was formed [134]. Geng et al. [135] indicated that the hardness tests performed after a laser modification of the alloy showed that the measurement of this parameter performed in the β -phase, yielded lower values of hardness than in the α -phase. The results for the β -phase were characterized by large deviations for the elastic modulus due to the small thickness of the β -grains and the presence of α -grains. In studies [136,137] it has been shown that as a result of rapid cooling of a material at the surface after treatment, a martensitic phase with the addition of the β phase is formed, while deep into the material a decrease in the compactness of the martensitic phase is observed, and the α phase tends to become dominant. A comprehensive analysis of the phase transformation in a Ti-64 titanium alloy subjected to an Nd:YAG laser modification was carried out in [138]. The presence of a melted zone and a heat-affected zone after laser treatment were marked and they had different microstructural characteristics. The melted zone was characterized by the presence of martensitic plates throughout, while the heat-affected zone, which was far from the laser source, contained short-rod β particles, martensitic plates and untransformed bulk in its microstructure. It was shown that the change in hardness during laser treatment was influenced by the presence of martensitic plates in the melted zone and a reduction in the grain size. The formation of the martensitic phase limited the diffusion of alloying elements, which directly led to the hardening of the surface structure. The study of [138] presents the preliminary results of values for hardness, using a calculation method and a measurement method. For both methods, the hardness increased with respect to the material without a laser treatment. The hardness for the melted zone was higher than for the heated affected zone and the differences in the hardness values were due to the fact that the calculation method did not take into account the occurrence of coarse α grains in the heated zone, while it was also difficult to take into account the contribution of the individual phases of the material in the zones [138].

The authors of [125] further observed the formation of a large number of dislocations and mesh distortions on the surface of a sample, increasing the hardness of the material. In the melted zone, the formation of nanotwins was observed, which slowed down the dislocation movements, and this had an additional hardening effect on the material [138,139]. It was indicated that reducing the grain size increased the hardness of the material [109]; however, after laser treatment, the grain size of the material increased while the hardness increased, suggesting that the grain size does not significantly affect the hardness as much as the dislocations formed and the phase transformations of the material [140]. In the work of [141], it was indicated that an increase in the amount of oxygen due to a femtosecond laser treatment resulted in an increase in the hardness with a concomitant increase in the brittleness of the material. Applying laser texturing to the surface linearly and performing dimple patterns resulted in an increase in the nano-hardness from 2 GPa for the base material to 4 GPa and 6 GPa, respectively, as tested by nanoindentation. The hardness obtained for each test was dependent on the type of laser selected and the processing parameters chosen. In paper [142], a pulsed laser treatment was performed using two different laser power parameters, and the modified samples were divided into two regions. It was shown that the region of the sample modified with a higher laser power of 3.99 W had a higher hardness than the region modified with a laser power of 1.71 W. In addition, it was shown that for treatment with the lower laser power, no significant difference in the hardness were registered between the remelted layer and the native material. The research of [143] indicated that a laser modification with a low laser power did not increase the hardness of the material as much as in the case of a high laser power, for the reason that a lower power also means less heat and there is not as much formation of the martensitic alpha phase after remelting. A high laser power is directly related to the rapid cooling of the material and as a result the formation of the martensitic alpha phase. In the work of [144], the formation of a TiO₂ rutile and anatase phase was demonstrated, and it was indicated that the amount of oxygen molecules present in the

structure depended on the laser modification method, namely, the type of laser and the parameters used. Pan et al. [145], as a result of their conducted research, indicated that the observed increase in the microhardness of the samples subjected to laser treatment was also because with an increase in the laser operating parameters there is an increase in the pressure. It was noted that an overly high value of the laser operating parameters was not able to effectively improve the microhardness of a surface [146], and this was because the yield strength of the titanium alloys had been exceeded [145]. The laser modification primarily increased the microhardness at the surface of the material, and the decrease in the hardness values was a gradient with an increasing test depth [145]. The change of the laser wavelength from 532 nm to 1064 nm showed a huge increase in the surface roughness which had a negative impact on the corrosion properties [147].

Table 4. Microhardness and hardness after laser treatment on titanium and its alloys.

Material	Microhardness and Hardness After Laser Treatment	Laser Parameters							References	
		Type of Laser	Energy/Laser Power	Impact Time	Pulse Duration	Frequency	Scan Speed (Mm/S)	Laser Pulses		Environment
Ti35Nb10Ta	3.8 GPa	Nd:YAG	1000 W	-	-	-	6.67 mm/s	-	Helium	[120]
	3.3 GPa		1500 W	-	-	-	10 mm/s	-		
	untreated material: 3.06 GPa	-	-	-	-	-	-	-	-	[148]
Ti30Nb4Sn	3.5 GPa	Nd: YAG	1000 W	-	-	-	the authors	-	Helium	[120]
	3.3 GPa		1500 W	-	-	-	6.67 mm/s	-		
	untreated material 2.44 GPa:	-	-	-	-	-	-	-	-	[149]
	4.9 GPa	Nd: YAG	50 mJ	-	-	10 Hz	-	-	Argon	[105]
Ti6Al4V	3, 4.01 for 150 µJ, 2.59 GPa for 240 µJ	femtosecond laser	10–240 µJ	-	290 fs	50 kHz	-	-	-	-
	3.84 GPa		Nanosecond Laser	1 s	-	-	-	-	-	[145]
Ti6Al4V	294 GPa	Shock Peening (LSP)	4 J	3 s	20 ns	1 H	-	-	-	-
	4.02 GPa		Nd:YAG	165 W	-	-	14 Hz	-	-	[124]
Ti6Al4V	2.45–3.43 GPa	-	-	-	-	-	500–18,000	-	[146]	
Cp-Ti	untreated material: 1.08 GPa	-	-	-	-	-	-	-	-	[122]
	2.59 GPa	Nd: YAG	100 W	-	5 ms	20 Hz	8 mm/s	-	-	-

6. Wear Resistance and Fatigue Behavior

An appropriate approach to improving wear resistance at present is to design alloys based on their chemical composition. In parallel, several technologies have been developed to prepare a modified layer with a high wear resistance [150]. The literature indicates that the direct effect on wear resistance is related to the hardness of a material [107,151]. One of the few disadvantages of titanium and its alloys is a low wear resistance [115]. For these materials, the need to improve this property is widely discussed [11,152] because the low wear resistance is a limitation of the various applications. Significant differences in the wear resistance of the various titanium alloys are indicated depending on the α , β , or $\alpha\beta$ type [150,153]. The literature points to a low wear resistance, especially in the case of titanium alloys β [92], for example, Ti-5Al-5Mo-5V-1Cr-1Fe [133], Ti-35Nb-7Zr-5Ta [154], and Ti10V2Fe3Al [155].

The literature reports that laser surface modification is a simple method to improve the wear resistance of a material [119,156–159]. In the research by Cheng et al. [133], despite an increased surface hardness after laser modification, no improvement in the wear resistance of the titanium alloy Ti5Al5Mo5V1Cr1Fe was observed.

The papers of [160,161] indicated that laser treatment in a nitrogen environment caused the formation of TiN, which significantly improved the surface hardness and wear resistance of the materials. The increased wear resistance was explained by a decrease in the coefficient of friction [160]. The research of [161] indicated that the relative wear resistance increased by 1.7 times compared to a material without a laser treatment. Moreover, the literature of [158] indicated that a TiN layer formed as a result of remelting in the presence of nitrogen, had a higher hardness and wear resistance than treated titanium alloys.

A study of the effect of laser processing on the wear resistance of pure titanium was carried out in [162], where laser processing was shown to reduce the weight loss of samples during a dry wear test. The study confirmed Archad's theory, that the wear rate is reversely proportional to the hardness [162,163]. The results of [162] for wear resistance indicated that the mass loss for a samples subjected to laser modification was much lower than for material without treatment, and that the wear indices for selected modified samples were practically constant, while for unmodified samples they increased significantly. The samples were subjected to a study of the change in the coefficient of friction during normal loading for increasing loads and the results in the cited work [162] indicated that the pure titanium samples without a modification showed a higher wear and material loss with an increasing normal load, while for modified samples a decrease in the wear was observed with increasing loads. In the work of [164], an increase in the wear resistance was observed in untreated material, while an increase in the load during the experiments lowered the wear resistance. The laser treatment created defects and when the load was applied, the structures were compressed, which increased the wear resistance because the material did not detach from the surface. It was shown that when the maximum temperature reached during the thermal cycle was higher than the melting temperature, a phase change to the martensitic phase occurred, and the fatigue strength and wear resistance of the material were improved; thus, this procedure is also used in the hardening of steels and cast irons [137].

The study results of Zeng et al. [165] also indicated that a laser treatment improved the wear resistance of a material, that the diagram of the dependence of a material loss volume on the wear time for both a non-laser treated and treated material was linear, except for modified samples where a small mass loss was observed, and that it was 37 times lower than the wear of the raw material. The ion release tests carried out showed that the increased wear resistance determined the reduced release of vanadium, which is a toxic element.

In the study of [166], as a result of laser modification, the formation of TiC was observed and it was indicated that the presence of this composite improved the hardness and wear resistance. It was shown that short laser processing times were more advantageous because the melted layer was more homogeneous. Moreover, increasing the laser processing time increased the hardness and surface roughness but the TiC structure was more uneven and hard TiC particles acted as an abrasive tool. The low speed of the laser beam on the material, causing the formation of deeper melts, also had a beneficial effect on increasing the wear resistance of the material.

In paper [167], an XRD study of a Ti834 alloy subjected to modification was carried out, where the fatigue strength (high cycle fatigue) was tested. It was shown that for modified samples there was an increase in the tested strength, which was justified by the formation of compressive stresses after laser shock peening. Jia et al. [168] confirmed that in this type of laser processing, compressive stresses are induced in the sample and increase with an increasing impact time. A 1998 study [169] showed that laser modification combined with previous coating applications allowed for a reduction in the adhesive and abrasive wear.

The researchers of [170,171] compared the treatment of titanium by ion implantation and laser nitriding. It was shown that the use of a CO₂ laser in a nitrogen environment allowed a reduction in the friction between the tested surfaces, with a concomitant

decrease in the fatigue strength [171]. Another study [170] evaluated the fretting fatigue behavior of a titanium alloy. It was observed that due to the formation of a heterogeneous, brittle surface after machining during fretting, the surface of the titanium alloy was unable to accept the loads set during fretting. Current literature [172–174] also shows that the use of laser modification is associated with decreasing the fatigue strength in titanium alloys. It is indicated that the fatigue strength is reduced by up to 30% compared to the very good fatigue strength of titanium alloys [172,175]. Additionally, it was indicated that with the increase in surface roughness after laser treatment, the cracks occurring on the surface generate a reduction in the fatigue strength. The resulting surface damage was identified as crack initiation sites [174]. The untreated material had crack initiation sites at the edges of the material, while in the case of the laser-treated material, the initiation site was in the center of the material [173].

7. Conclusions

The literature review focused on the effects of laser modification without material gain on titanium and its alloys. The presented work provides a comprehensive knowledge base on the effects of a fiber laser, Nd: YAG, Yd: YAG laser, and femtosecond laser and the shock peening method on selected properties of the titanium materials used in the medical industry. The paper discusses such properties as the roughness, wettability, resistance to corrosion, wear, and fatigue, as well as the effect of laser modification on material hardness.

1. The first section focused on the surface roughness and wettability, allowing us to assess the impact of laser modification with different types of lasers, which led to the conclusion that the use of this type of modification increases the surface roughness and that it varies depending on the operating parameters of the lasers.
2. The wettability of a surface is a topic that is widely discussed due to the fact that laser modification affects the change in the nature of the surface. Notably, a large impact on the hydrophilicity or hydrophobicity of a surface is the timing of the test in this direction, as well as the environment in which the samples are stored, but depending on the application of the material, there are different requirements, which does not indicate a more advantageous character.
3. Collected publications in the field of corrosion resistance research determine that the action of a laser beam on titanium materials improves the corrosion resistance, which is important because this reduces the release of dangerous elements from the implants.
4. Laser modification alters the micro- and nano-hardness for each type of laser. It is indicated that laser modification allows the process to be carried out in such a way that the hardness obtained after the change is close to that of bone.
5. The effect of laser modification on material wear was presented based on a collection of literature from a wide time range, which allowed the presentation of further opportunities to discuss the selection of optimal laser operating parameters, such as the laser operating power, laser beam density, and pulse duration.
6. In addition, the aspect of wear resistance was discussed, where it was shown that the use of laser modification improves this material property.
7. The presented review of the current literature on the subject provides a theoretical basis for studying the effects of laser processing on titanium and its biostops and for conducting targeted processing in the area where modification is needed to improve implants.
8. The presented review of the current literature related to the effects of laser modification on selected properties of titanium materials and provides a theoretical basis for the researchers' research.
9. The review indicates the need to deepen the research related to the wettability of the surface of titanium materials used in biomedicine, due to the fact that there is no clear

indication of which character of the surface is more favorable, and it is necessary to identify the areas of application of a hydrophobic and hydrophilic surface obtained by modification. In addition, it is important to focus on studies related to the durability of materials against wear and fatigue and corrosion because these two properties directly affect the length of stay of an implant in the body.

Author Contributions: Conceptualization, J.S. and M.S.; Methodology, J.S.; Formal analysis, M.S.; Investigation, J.S.; Writing—original draft preparation, J.S.; Writing—review and editing, J.S. and M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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