coatings

Review

Research Progress of Surface Treatment Technologies on Titanium Alloys: A Mini Review

Bingyu Xie * and Kai Gao *

School of Automobile and Traffic Engineering, Wuhan University of Science and Technology, Wuhan 430065, China
* Correspondence: xiebingyu@wust.edu.cn or bingyu_xie@163.com (B.X.); gaokai@wust.edu.cn (K.G.)

Abstract: Titanium alloys are important strategic structural materials with broad application prospects in the industries of aerospace, space technology, automobiles, biomedicine, and more. Considering the different requirements for the diverse applications of titanium alloys, the modification of physicochemical properties, mechanical properties, and biocompatibility are required, including novel composite materials, novel design, novel manufacturing methods, etc. In this review, the surface treatment technologies utilized on titanium alloys are summarized and discussed. Regarding surface modification of titanium alloys, the methods of laser treatment, electron beam treatment, surface quenching, and plasma spraying are discussed, and in terms of the surface coatings on titanium alloys, thermal spraying, cold spraying, physical vapor deposition, and chemical vapor deposition are also summarized and analyzed in this work. After surface treatments, information on microstructures, mechanical properties, and biocompatibility of titanium alloys are collected in detail. Some important results are summarized according to the aforementioned analysis and discussion, which will provide new thinking for the application of titanium alloys in the future.

Keywords: surface treatment; titanium alloys; microstructure; physicochemical properties; mechanical properties

check for updates

Citation: Xie, B.; Gao, K. Research Progress of Surface Treatment Technologies on Titanium Alloys: A Mini Review. *Coatings* **2023**, *13*, 1486. https://doi.org/10.3390/coatings13091486

Academic Editor: Alexander Tolstoguzov

Received: 19 June 2023
Revised: 31 July 2023
Accepted: 17 August 2023
Published: 23 August 2023

1. Introduction

Titanium alloys have been widely used in the fields of aerospace, metallurgy, chemicals, petroleum, medicine, and other industries, and are considered to be the most promising metal materials due to their low density, high specific strength, high corrosion resistance, and other excellent characteristics [1–5]. However, during the process of manufacturing and subsequent treatments, the generated tensile stresses may cause the fatigue properties of titanium alloys to deteriorate [6]. Some researchers have shown that this fatigue failure often initiates from the surface [6,7], and the surface integrity and the surface stress could effectively improve the resistance to fatigue failure [8]. Thus, the surface properties are very important to titanium alloys' application, including the surface residual stress, the surface hardness, the surface friction properties, the surface corrosion resistance, etc.

The surface treatments of titanium alloys are very important methods needed to improve their unfavorable properties [9–11], and include physicochemical treatment methods and mechanical treatment methods. Physicochemical treatment methods mainly include surface physical vapor deposition (PVD) [12,13], chemical vapor deposition (CVD) [14,15], surface boriding [16–18], carburizing [19], nitriding [20–22], etc. Mechanical treatment methods mainly include surface laser treatment [23–25], surface shot peening [26–28], and others. The previous development of surface treatments for titanium alloys occurred starting from the initial traditional stage (a single mechanical treatment method) and the middle stage of modern surface technology (a single physicochemical treatment method), and now, surface treatment technologies for titanium alloys are being developed using a variety of technologies for comprehensive application. Therefore, the recent progress in the field of surface treatment methods for titanium alloys are reviewed and discussed in this paper from six aspects.

(1) Surface biochemical treatment of biomedical titanium alloys.
(2) Surface nitriding and nitrocarburizing on titanium alloys.
(3) Hybrid surface modification (HSM) on titanium alloys.
(4) Electrochemical/chemical surface treatment of titanium alloys.
(5) Laser surface modification of titanium alloys.
(6) Surface mechanical treatment on titanium alloys.

Through our analysis of the above six aspects, we hope to obtain the collection of the surface treatment technologies for titanium alloys and to provide new thinking for the application of surface treatments in the development of titanium alloys.

2. Recent Developments of Surface Treatment Technologies for Titanium Alloys

2.1. Surface Biochemical Treatment of Biomedical Titanium Alloys

Regarding surface treatment on biomedical titanium alloys, Wang et al. [29] deposited TiO_2 nanotube coatings on a Ti-6Al-4V substrate by means of anodic oxidation and found that the microhardness and elasticity modulus of the coatings decreased as the oxidation time increased, which is beneficial, as it reduces the possibility of stress shielding and improves the biomechanical compatibility. Tan et al. [30] modified the Ti-Zr binary alloys for dental implant materials via sandblasting and sulfuric acid etching, and lower cell attachment levels were observed on Ti-50Zr. The content of Zr influenced the surface properties of Ti-Zr alloys (as shown in Figure 1). The wettability variation of Ti-Zr alloys was verified by the contact angle of water, which on each sample clearly increased from day 14 and day 28 (in Figure 1a,b). Additionally, Figure 1c indicates the fluorescence microscopy of cells stained with calcein, which confirmed the positive and negative effects of Zr alloys on the cells depending on the Zr proportion. The cell attachment level is shown in Figure 1d. In order to improve the osteogenetic and antibacterial properties of Ti-based implants for orthopedic applications, Liu et al. [31] fabricated TiO_2 nanotube arrays covered with chitosan/sodium alginate multilayer films on titanium substrates, which were able to accelerate the growth of osteoblasts via cytocompatibility evaluation in vitro. Receiving inspiration from the slippery surface of the Nepenthes pitcher plant, the lubricated orthopedic implant surface (LOIS) was introduced by Chae et al. [32] to modify the surface properties of orthopedic implants, and the LOIS showed a long-lasting and extreme liquid repellency against diverse liquids and biosubstances (in Figure 2). Figure 2 shows the antibiofouling property of LOIS against bacteria, cells, protein, and calcium. Bionic structures have always been an important research area in the manufacturing and materials industry, and surface treatments are similar. Many research aims can be achieved with the help of plant-based surface structures such as the surface of the lotus leaf.

Based on high-performance organisms in nature, multi-phase, multi-level, and multi-scale hybrid reinforcements were deposited onto the surfaces of titanium alloys by Bai et al. [33]. Ren et al. [34] utilized a method combining ultrasonic acid etching with anodic oxidation to modify the surface of electron-beam-melting Ti-6Al-4V implants, and the hierarchical micro-/nano-structure was beneficial for cell adhesion and expansion, which significantly promoted cell proliferation and enhanced cell differentiation behaviors as well. Peng et al. [35] fabricated the micro-textures and diamond-like carbon (DLC) coatings on the titanium alloy surface using laser and magnetron sputtering technology, and the best tribological properties were obtained: a friction coefficient of 0.0799 was achieved, and the wear volume was decreased by 97.5%. The surface microstructure and the tribological properties are indicated in Figure 3, and the friction coefficient of the titanium alloy surface with textured coatings is significantly decreased as the wear resistance is effectively improved. Meanwhile, micro-textures with appropriate density and depth could further improve the friction coefficient of textured DLC coated surface. Todea et al. [36] investigated the effects of different surface treatments on the bioactivity of porous Ti-6Al-7Nb implants manufactured via selective laser melting. The materials produced by different treatment methods were validated by the self-assembly of an apatite-type layer when the bioactivity was tested in simulated body fluid (SBF). Zhang et al. [37] introduced some advanced surface-modification technologies such as additive manufacturing, selective laser melting, etc. Cui et al. [38] prepared a nanocrystalline TiN-graded coating on Ti-6Al-4V using the DC (direct current) reactive magnetron sputtering method. The surface nanohardness reached 28.5 GPa and the tribocorrosion resistance increased by 100 times compared to the substrate, which demonstrated good corrosion and wear resistance. Different treatment methods introduce different surface microstructures, which will cause the variation of surface mechanical properties and biocompatibility and influence the application of titanium alloys in the biological field. For instance, coatings with high hardness and high toughness could be obtained via coupling and multi-functional response mechanisms between different phases. Some special structures on the surface, as the micro/nano-structure, could promote cell proliferation and enhance cell differentiation behaviors. The surface fine texture could show favorable anti-friction and wear-resistance effects.

The aim of applying surface treatments to biomedical titanium alloys involves the friction and wear properties of treated materials. In addition, the physicochemical properties and biocompatibility of the treated titanium alloys should also be considered in order to obtain more combinations of properties. Although some better results have been obtained with surface treatments of biomedical titanium alloys, such as the nanocrystalline surface structure, the micro/nano surface structure, the laser surface treatment, etc., they were obtained under some special conditions, such as in the laboratory. The popularization and application of some new surface structures need to be further developed, such as the micro/nano surface structure mentioned above.

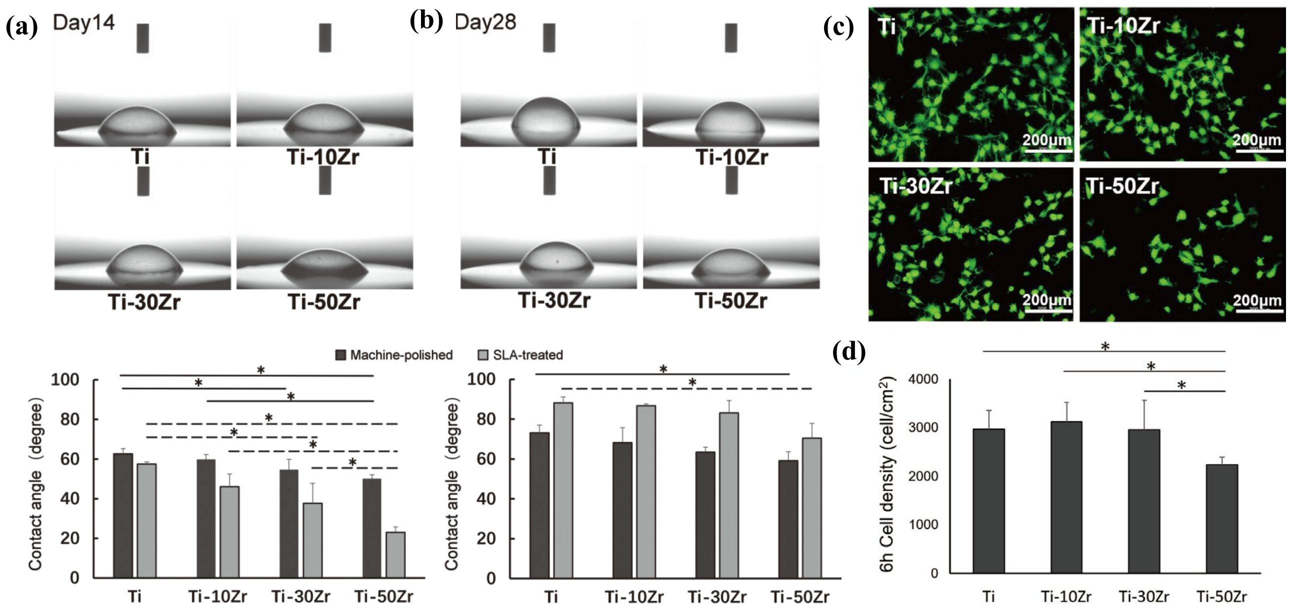

Figure 1. The wettability of Ti-Zr alloys after 14 days (**a**) and 28 days (**b**). Data are expressed in mean ± SD values (n = 5). * $p < 0.05$ indicates a statistically significant difference among the c.p. Ti and Ti–Zr alloy surfaces; (**c**) fluorescence microscopy images of osteoblastic cells stained with calcein after 6 h of culture; (**d**) osteoblastic cellular attachment level, evaluated by fluorescence images. Data are expressed as mean ± SD values (n = 5 × 3 disks.) * $p < 0.05$ indicates a statistically significant difference between the c.p. Ti and Ti–Zr alloy surfaces [30]. (Reused with permission from ref. [30]. Copyright 2022, The Japanese Society for Dental Materials and Devices).

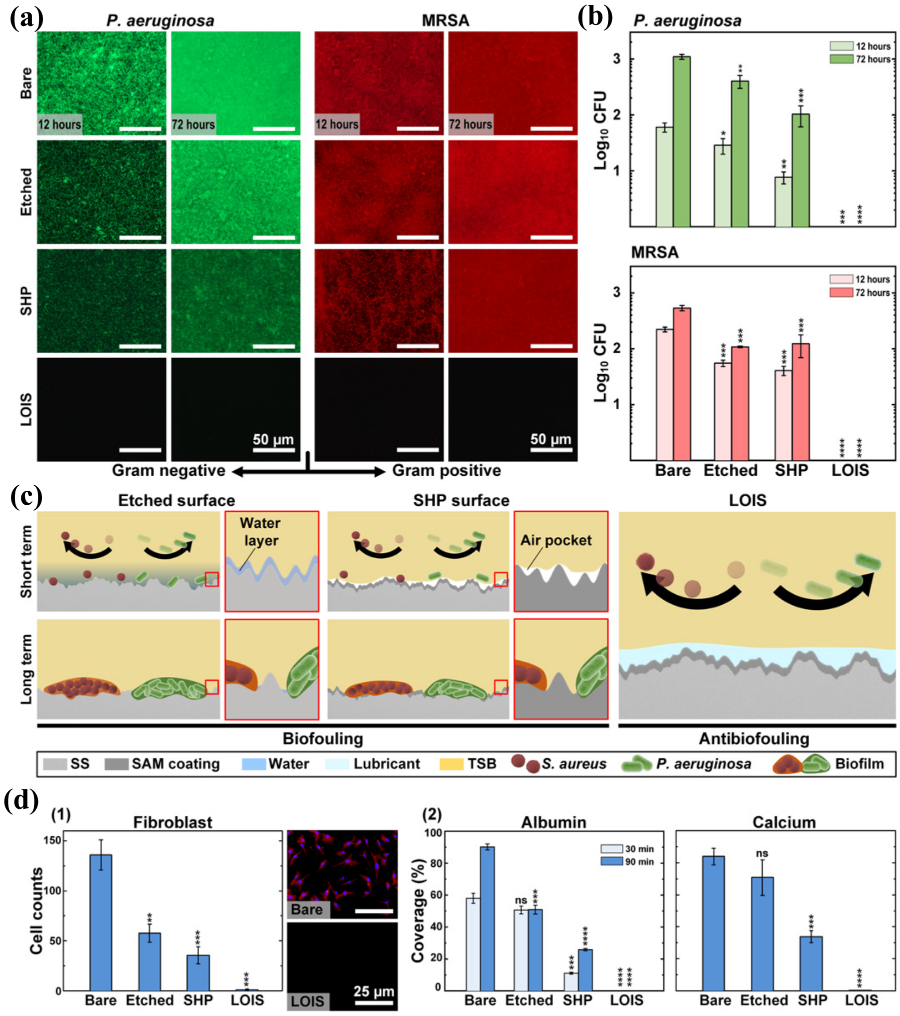

Figure 2. Antibiofouling property of LOIS against bacteria, cells, protein, and calcium. (**a**) Fluorescence microscopy images of each group (bare, etched, superhydrophobic, and LOIS) incubated in *P.* (**b**) The number of adherent colony-forming units of *P. aeruginosa* and MRSA on each group of surfaces. (**c**) Schematics for the antibiofouling mechanisms of etched, superhydrophobic, and LOIS in the short and long term. (**d**) (1) Number of fibroblasts adhered on each substrate and fluorescence microscopy images of the cells adhered on bare and LOIS. (2) Adhesion test for immune-related protein, albumin, and calcium involved in the bone healing process. (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, and **** $p < 0.0001$) [32] (Reused with permission from ref. [32]. Copyright 2020, AAAS publications. Open access article CC BY-NC-ND).

2.2. Surface Nitriding and Nitrocarburizing on Titanium Alloys

The surface treatments of nitriding and nitrocarburizing are popular surface treatment methods for metal materials. Takesue et al. [39] utilized gas blow induction heating (GBIH) to modify the surface microstructure, and the disappearance of the passivation film was caused by the diffusion of oxygen atoms in the passivation film into the substrate. Zhang et al. [40] fabricated core-shell-structured Ti alloys via spark plasma sintering (SPS) with high yield strength (~1.4 GPa) and high thermal stability, which was ascribed to the hard Ti-N shells and the soft Ti cores. Figure 4 indicates the schematic diagram of the core-shell structure, and the formation of this structure can be attributed to occurrence of α and β phase transformations, in contrast to the gradient structure, which has not experienced phase transformations. Li et al. [41] investigated the friction and wear behaviors of Ti/Cu/N coatings on titanium alloys using direct current magnetron sputtering, and the wear resistance of the coatings was obviously improved while the content of Cu reached 10.98 at%. Takesue et al. [42] found that the decrease in Ti-6Al-4V fatigue strength was ascribed to the higher Young's modulus of the compound layer and the grain coarsening of the α-phase. After removing the compound layer formed by GBIH nitriding, the fatigue properties were improved. The microstructure of the fracture surface is shown in Figure 5. Furthermore, the combination of GBIH-nitriding and fine-particle-peening (FPP) pre-treatments improved the wear resistance, because FPP promoted the diffusion of the nitrogen into titanium [42]. Via laser irradiation of pure graphite powder in a nitrogen environment, Seo et al. [43] achieved carbonitriding on a Ti-6Al-4V surface, and Ti (C, N) compounds were formed in the hardening layer on the surface, which was ascribed to the high thermal conductivity of graphite, and it enhanced heat transfer between the laser source and the substrate.

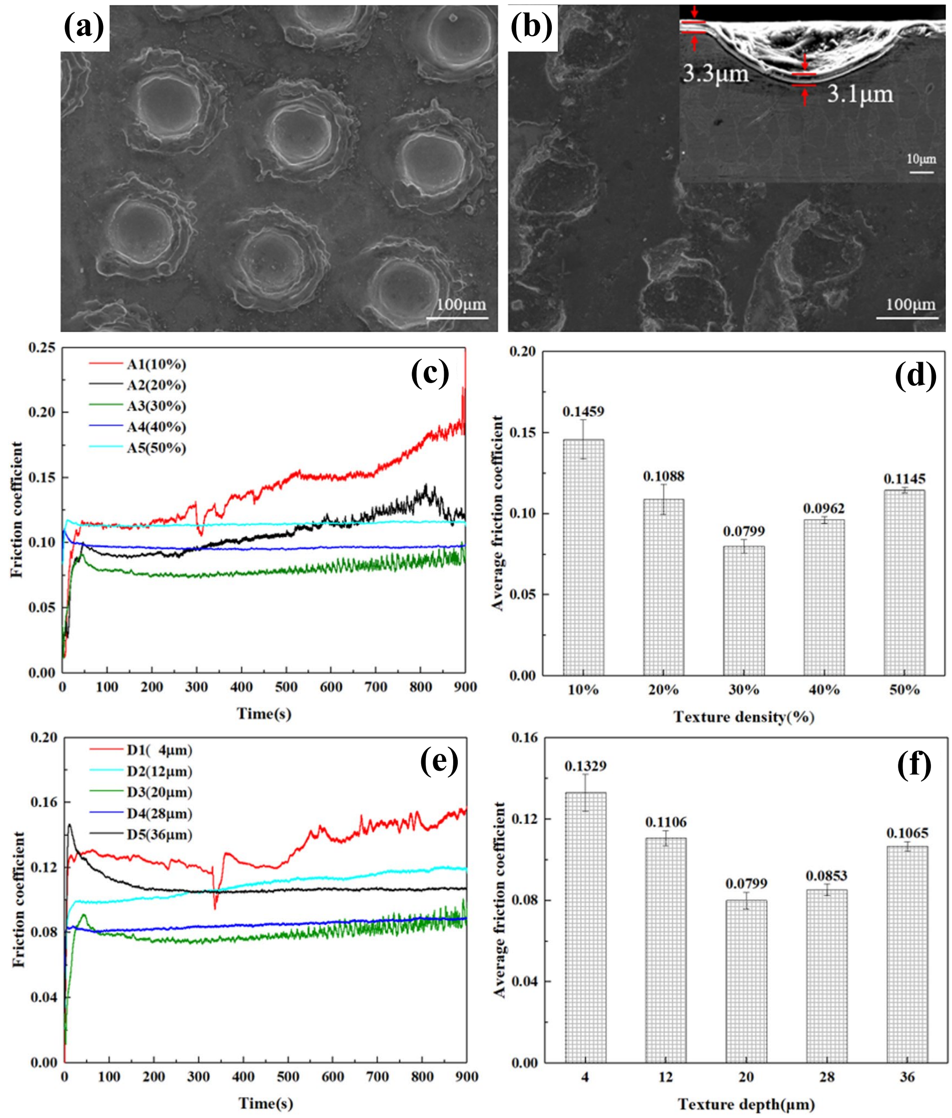

Figure 3. SEM image and EDS analysis of samples: (**a**) textured titanium alloy sample; (**b**) textured diamond-like carbon (DLC)-coated sample. Friction coefficient of samples with different texture densities; (**c**) friction coefficient curve; (**d**) average value of friction coefficient; different texture depths; (**e**) friction coefficient curve; and (**f**) average value of friction coefficient [35] (Reused with permission from ref. [35]. Copyright 2020, IOP Publishing).

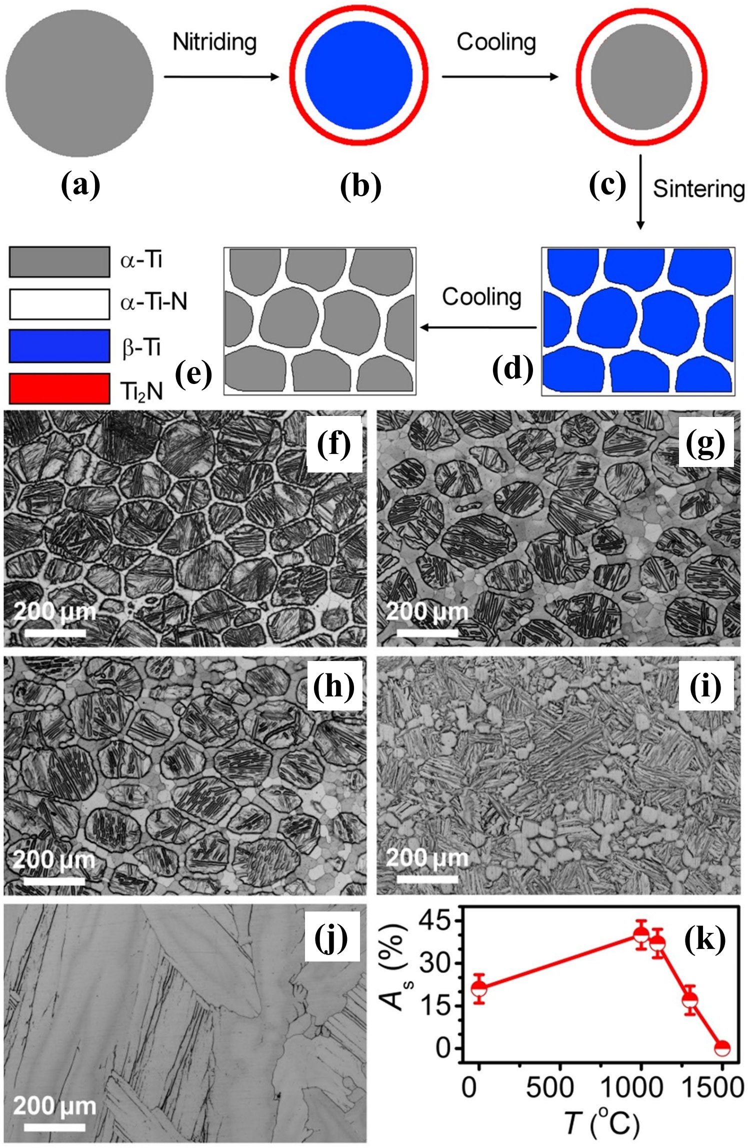

Figure 4. The formation process of the core–shell Ti-N alloys during the nitriding (**a**–**c**) and SPS sintering (**c**–**e**) processes. Microstructure variation of the SPS-sintered specimen: (**f**) before annealing; (**g**–**j**) those annealed under 1000, 1100, 1300, and 1500 °C; (**k**) variations of shell area fraction A_S versus annealing temperature *T*. [40] (Reused with permission from ref. [40]. Copyright (2017), Springer Nature).

Based on the influence of nitriding and nitrocarburizing on the surface, GBIH nitriding showed the ability to modify the surface microstructure of Ti-6Al-4V within a short time. Some novel treatments, like laser carburizing, laser nitriding, and laser carbonitriding, were introduced, and larger hardness and greater hardening depth were tested after the carbonitriding process. The surface treatments of nitriding and nitrocarburizing can improve the strength and hardness of the surface layer. This is due to the diffusion and carbonitriding reaction of carbon and nitrogen atoms, because reactions occur easily between Ti, C, and N atoms. Although the nitrocarburizing provides a pathway towards the advanced material which combines high strength, good plasticity, and better thermal stability, the influence of the hardening layer's depth on the surface properties is still a difficult point needing to be resolved. Because there are too many complex factors affecting the hardening layer depth, even the current study is difficult to conduct thoroughly and completely.

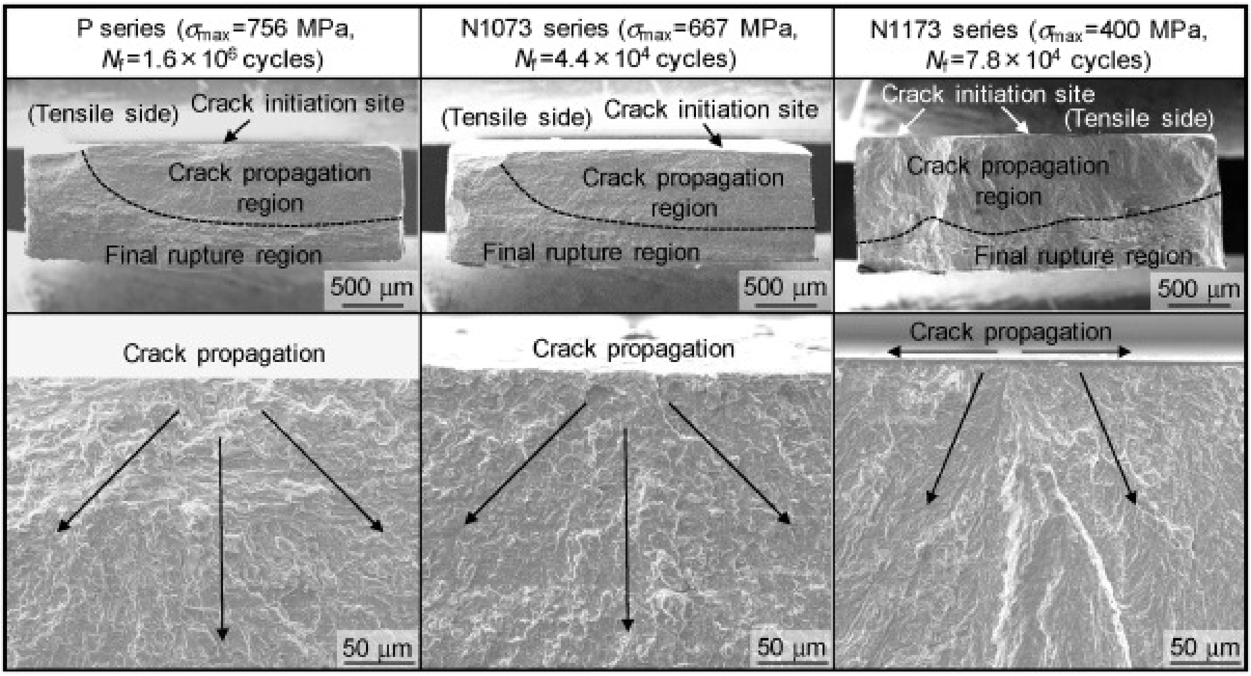

Figure 5. SEM micrographs of the fractured surfaces of failed specimens that were polished (P series) and induction-heated at 1073 K (N1073 series) and 1173 K (N1173 series) in nitrogen [42]. (Reused with permission from ref. [42]. Copyright 2020, Elsevier).

2.3. Hybrid Surface Modification (HSM) on Titanium Alloys

Different surface treatment methods have different advantages, a variety of which can be utilized to maximize their advantages. In the work by Zammit et al. [44], an HSM treatment combining shot peening and the deposition of a tungsten-doped diamond-like carbon coating (WC/C) via PVD on the Ti-6Al-4V surface was developed, with a high surface hardness of 12.79 GPa. In the work by Zhang et al. [45], a novel packed-powder diffusion coating (PPDC) technique was utilized on the surfaces of Ti alloys, and a controllable Al_3Ti intermetallic-based composite coating was formed, which resulted in a significant increase in the oxidization resistance of the Ti alloys. The application of the ultrasonic nanocrystal surface modification (UNSM) technique for strengthening the surfaces of titanium alloys was introduced [46]. The schematic and mechanism of UNSM are shown in Figure 6. Special surface structures like the tracks and the micro-dimples are introduced on the surface, which can improve the surface hardness and the fatigue properties. Via electron beam boriding and composite alloying of titanium alloys and steels, wear-resistant coatings were obtained in Baris' work [47], and the main effect influencing the structure of the coating and its hardness was the effective concentration of alloying elements. Casadei et al. [48] synthesized a Ti/TixNy composite coating on Ti-6Al-4V utilizing a new layered coating system, including the reactive-plasma-sprayed/arc-deposited method. Li et al. found that a surface layer consisting of TiO_2 and TiN was introduced in Ti-6Al-4V via a new surface treatment process based on simultaneous nitriding and thermal oxidation, and the coating fabricated under 800 °C showed the best mechanical properties and corrosion resistance [49].

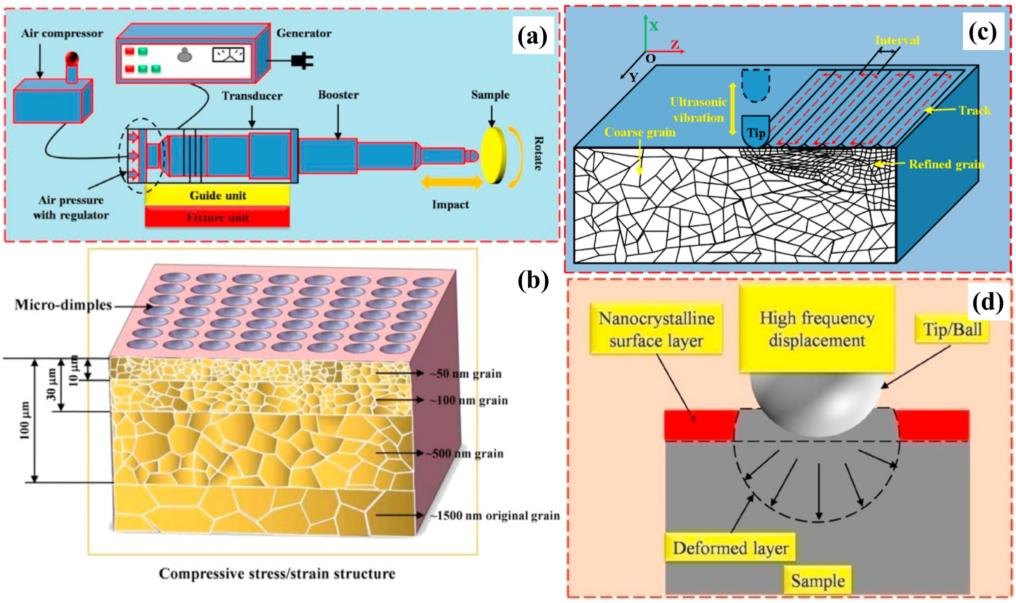

Figure 6. (**a**) Experimental installation diagram of the UNSM technique; (**b**) schematic of the microstructure of the modified layer under UNSM; (**c**) schematic diagram of UNSM; (**d**) schematic diagram of continuous UNSM processing. [46]. (Reused with permission from ref. [46]. Copyright 2021, Elsevier).

Tarbokov et al. [50] manufactured a titanium alloy surface with a typical micro-roughness height of 2–4 µm via a successive mechanical treatment and irradiation with powerful ion beams (PIB). The machining and PIB were conducted at 1.5 J/cm^2 in a pulse, which was able to improve the adhesion properties of the titanium alloys for application in the medical field. In the work of Takesue et al. [51], nitrided layers with high hardness and compressive residual stress were obtained, which were able to obviously improve the wear resistance and fatigue strength. This was ascribed to the diffusion of nitrogen atoms during nitriding and the fine particle peening. Zammit et al. [52] improved the adhesion and fatigue characteristics of Ti-6Al-4V after shot-peening pre-treatment followed by the deposition of a WC/C coating via PVD. The residual stresses measured on the shot-peened samples reached a maximum of −764 MPa at around 12 µm below the surface and prevailed up to a depth of slightly higher than 75 µm. Song et al. [53] adopted a type of plasma spray–physical vapor deposition technology to synthesize TiN coatings on Ti-6Al-4V, and the longer heating time, lower substrate temperature, and decreasing reactant concentration influenced the hybrid structure of the TiN coating. With increasing spraying distance, the average hardness (*H*) and elasticity modulus (*E*) of TiN coatings decreased from 16.3 to 13.4 GPa and from 234.2 to 202.9 GPa, respectively. However, the average *H* and *E* of coated Ti-6Al-4V increased to 5.81 and 132.3 GPa, respectively.

Compared with a single treatment method, hybrid surface treatment can allow for better surface performance to be attained and can also provide some special properties which are not available with a single surface treatment. Compared to the usual method of PVD deposition, the chemical reactions between the PVD film and the coating were beneficial for the graded properties and the outstanding adhesion of the multilayer system. Shot peening was able to improve the fatigue life with both LCF (low-cycle fatigue) and HCF (high-cycle fatigue), which was ascribed to the resistance effect of crack initiation due to the high dislocation densities and the resistance effect of crack propagation due to the compressive residual stresses. Combining shot peening with nitriding and nitrocarburizing, the tribological, fatigue-related, and biological adhibition of Ti alloys were further improved because of the advantages of both shot peening and nitrocarburizing.

Of course, hybrid surface treatment requires more complex treatments and preparation methods. Although HSM can bring many advantages, its equipment demands are more complex, and the parameters are more complicated as well. If researchers want to obtain optimal parameters, they need to spend more time exploring reasonable HSM parameters which can achieve the best surface performance.

2.4. Electrochemical/Chemical Surface Treatment of Titanium Alloys

Electrochemical/chemical surface treatment mainly utilizes chemical reagents to react with the metal surface, then generates a surface layer with special functions and special physical and chemical properties. After that, it can improve the physical, chemical, and mechanical properties of the material's surface. The electrochemical/chemical surface treatment method is one of the common methods for titanium alloy surface treatment. Hou et al. [54] used the plasma electrolytic oxidation (PEO) method to form ~12-micron-thick, uniform, adherent, and porous oxide coatings on titanium alloy surfaces under low voltages (120 V), which improved the hardness but introduced stress-induced cracking. Kesik et al. [55] found that alkali-treated oxide layers were formed and showed high bioactivity on anodized titanium alloys (Ti-15Mo, Ti-13Nb-13Zr, and Ti-6Al-7Nb) in Wollastonite suspension. The microstructures of the alkali-treated oxide layers in titanium alloys are shown in Figure 7. Based on the porous oxide layer formed on the titanium, it shows that the optimal condition for the oxide layers' treatment is at temperature of 60 °C for 8 h.

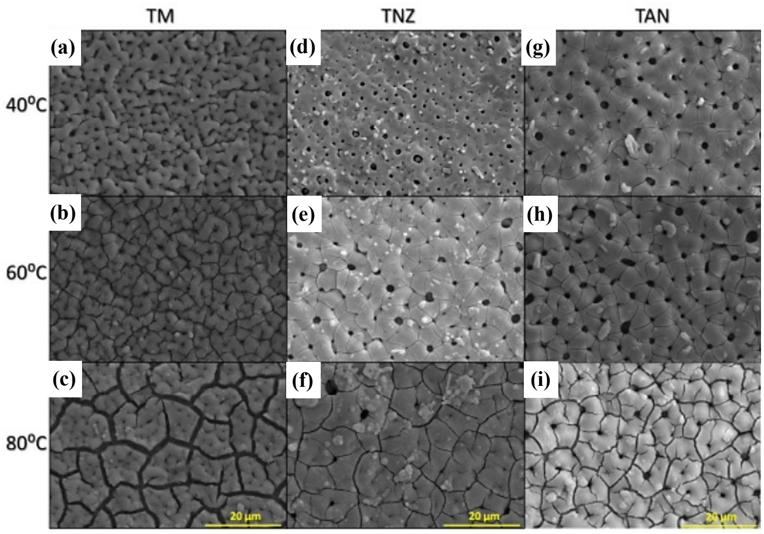

Figure 7. SEM images of Ti-15Mo (TM) (**a**–**c**), Ti-13Nb-13Zr (TNZ) (**d**–**f**), and Ti-6Al-7Nb (**g**–**i**) samples after anodization and immersion in 5 M NaOH at various temperatures for 8 h. [55] (Reused with permission from ref. [55]. Copyright 2017, MDPI).

In the work of Rudawska et al. [56], anodizing followed by vibratory shot peening was able to improve the strength of the titanium alloy sheet adhesive lap joints. This is because the vibrational shot peening increased the curing of the adhesive surface layer, which then increased the strength of the adhesive joint under variable force loads. Four different surface treatments were adopted on a Ti-35Nb-7Zr-5Ta surface by Vlcak et al. [57]. During the corrosion process, the charge transfer influenced the colonization ability of MG-63 cells on the surface, which was more important than other surface parameters (roughness, wettability). Some chemical surface treatments also show the advantages of improving the surface properties of titanium alloys. Khodaei et al. [58] used an H_2O_2 solution to treat the surface of a titanium dental implant, and it was found that the optimum treatment time was approximately 6 h in H_2O_2 solution at 80 °C, making it more suitable for dental implantation. Zhao et al. [59] investigated the doped thermochromic VO_2 film on a Ti surface via rapid thermal annealing (RTA), and a lower transition temperature of 44.9 °C and an extremely narrow hysteresis width of 2.36 °C were formed due to the smaller and more uniform surface particles. Figure 8 demonstrates the microstructures of VO_2 films with different Ti contents. With low Ti content, the scattered rod-shaped particles are formed (Figure 8a,b). After Ti doping, the size of the massive particles becomes significantly smaller, and the distribution of particles becomes uniform (Figure 8c,d). Figure 8e,f show that the thickness of the V film is 102 nm and that of the VO_2 film is 148 nm after RTA. Zhao et al. [60] utilized alkali treatments to adjust the microstructures of microarc-oxidized coatings of a Ti2448 titanium alloy, and the coatings showed excellent apatite induction properties when the concentration was less than 15 mol/L. Luo et al. [61] studied the adsorption properties of SO_2 gas on N-, Ti-, and N-Ti-doped graphene coatings using the density functional theory, and the N-Ti graphene coating was the most optimally adsorbent because of its low adsorption energy (−2.836 eV) and remarkable charge transfer, which is beneficial to the development of gas sensors to detect SO_2.

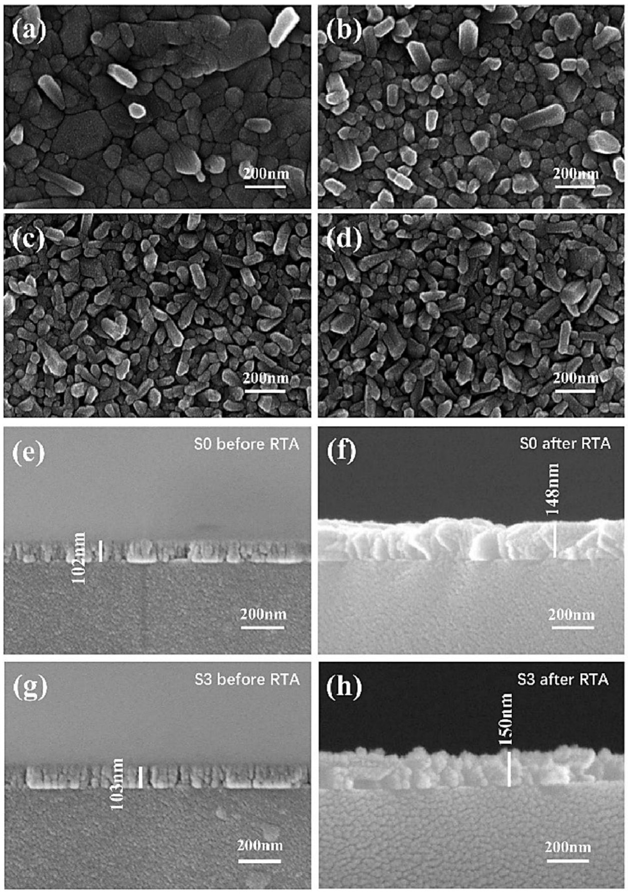

Figure 8. SEM photographs of VO_2 films with different Ti contents. (**a**–**d**) Samples with sputtering times from 0 to 6 min and Ti surface dopant contents from 0% to 0.43%, respectively; (**e**–**h**) the cross-sections of samples before and after rapid thermal annealing (RTA) [59]. (Reused with permission from ref. [59]. Copyright 2022, Elsevier).

Based on the discussion in this section, much work on electrochemical/chemical surface treatment has been focused on improving the physical and chemical properties of titanium alloy surfaces, as well as the application of titanium alloys as functional materials in corrosion resistance, surface free energy variation, etc. In the field of electrochemical/chemical surface treatment, different surface treatment methods can be adopted to strengthen titanium alloy surfaces, including alkaline degreasing, anodizing, the PEO method, alkali treatments, H_2O_2 solution treatment, etc., which provides some simple ways to obtain a functional surface.

After electrochemical/chemical surface treatment, some oxides formed on the titanium alloys, which influenced the surface morphology and wettability and provided more nucleation sites for apatite when immersed in the simulated body fluid. The electrochemical/chemical surface treatment was able to improve the surface physicochemical properties;

the hardness of the coatings was improved, but stress-induced cracking was sometimes introduced, which may have reduced the corrosion resistance of the coatings. Consequently, the comprehensive properties of titanium alloys after electrochemical/chemical surface treatment should be considered, including hardness, corrosion resistance, etc. This can provide a theoretical and experimental basis for protecting the surfaces of light metals.

2.5. Laser Surface Modification of Titanium Alloys

Due to the good monochromaticity and high energy of lasers, they have been applied in many fields as special forms of energy. Research works investigating the surface interaction between lasers and titanium have been carried out for many years, especially regarding the influence of lasers on the microstructure and the mechanical properties of titanium alloys, which is still a hot topic of research now. Laser surface nitriding was utilized to modify titanium alloy surfaces for orthopedic implant applications, and Ti-35.5Nb-7.3Zr-5.7Ta (β_{Ti}) was the most appealing choice for joint replacement applications because of the higher mechanical compatibility found in the work of Shirazi et al. [62]. Guo et al. [63] utilized a nanosecond laser to fabricate the hierarchical structures of titanium alloy surfaces, and the micro-/nanostructures of the pitted surfaces showed superhydrophobic properties (as shown in Figure 9). The nanosecond lasers induced micron-sized grooves on titanium surface in the study by Wang et al. [64], as shown in Figure 10. This caused the cells to form a cytoskeleton with a high aspect ratio and limited the migration and spread of the cytoskeleton. The surface fine structure shown in Figures 9 and 10 reveals the advantages of a nanosecond laser; different structures can be obtained via adjusting laser energy and scanning spaces.

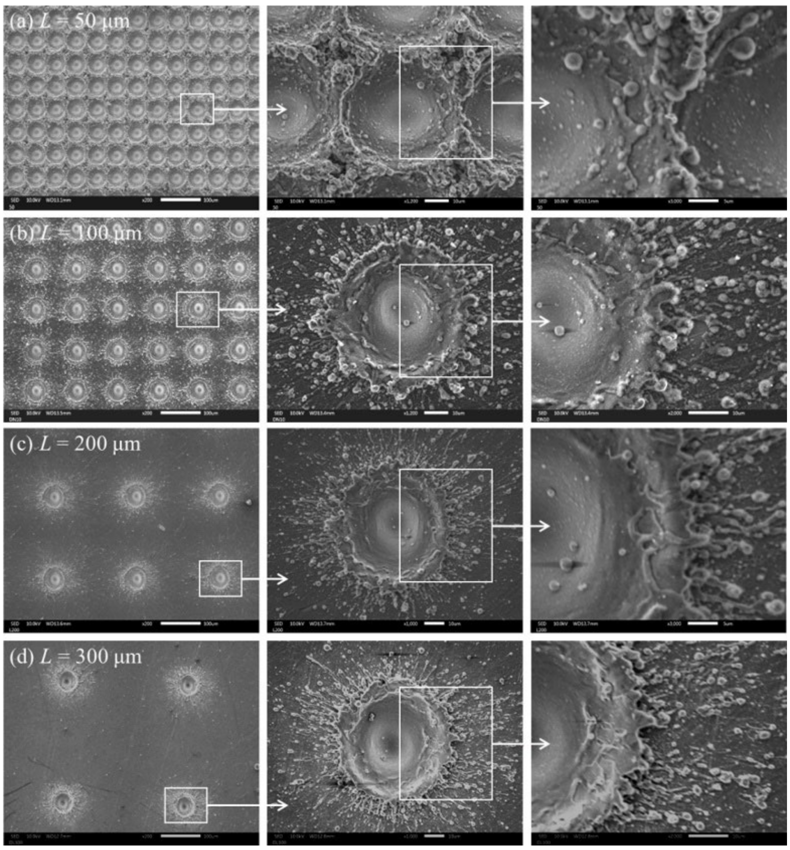

Figure 9. SEM images of the pitted surfaces of N = 10 processed with different scanning spaces. (**a**) L = 50 μm; (**b**) L = 100 μm; (**c**) L = 200 μm; (**d**) L = 300 μm. [63]. (Reused with permission from ref. [63]. Copyright 2021, Elsevier).

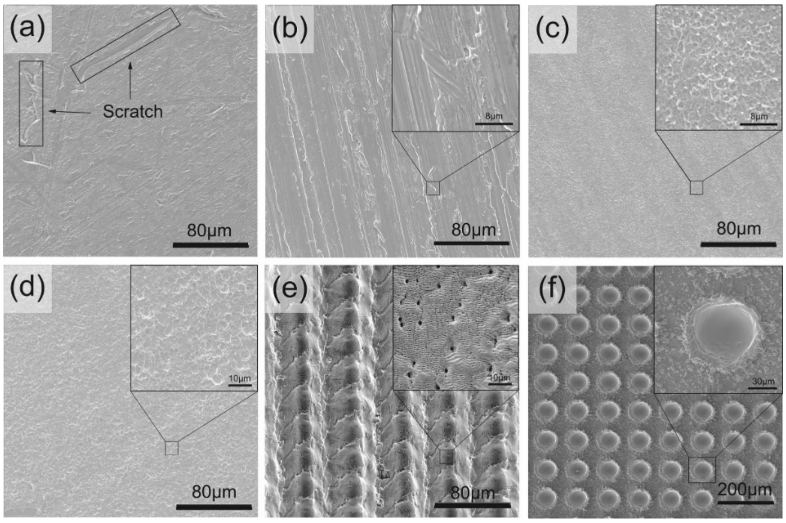

Figure 10. Surface microstructure after treatment. (**a**) Metallographic grinding; (**b**) parallel grinding; (**c**) diamond blasting and acid etching; (**d**) Al_2O_3 blasting and acid etching; (**e**) laser groove array; (**f**) laser pore array [64]. (Reused with permission from ref. [64]. Copyright 2020, Elsevier).

Laser shock peening was adopted in the work of Pan et al. [65] to introduce the refinement surface of Ti-6Al-4V, and the surface texture was transformed from a [0110] fiber orientation to a [1210] orientation. The dynamic recrystallization accompanying the finer grains was ascribed to the massive potential nucleation sites offered by shear bands. Additionally, nitrided layers on a titanium alloy's surface were formed via the laser nitriding method in the work of Yao et al. [66], and the hardness of the nitrided layer was more than 9 GPa. The combined effect of laser texturing and carburizing improved the wettability and specific surface area of a Ti-6Al-4V surface in Dong et al.'s work [67], providing a mechanical self-locking and matching chemical property between the substrate and diamond-like carbon film coatings. Han et al. [68] added Cu in Ti-6Al-4V wires via directed energy deposition, and the formation of Ti_2Cu nano-particles and refined grains improved both the strength and the plasticity of Ti-6Al-4V-8.5Cu. The grain refinement was the main strengthening mechanism after adding Cu. Pan et al. [69] investigated the femtosecond laser-induced surface modification of Ti-6Al-4V. The surface's compressive residual stress reached −746 MPa, and the hardness was improved by 16.6%. The wear mass loss and the average coefficient of friction (COF) after treatment were reduced by 90% and 68.9%.

The results in this section indicate that laser surface treatment is a very popular surface treatment method, especially in the preparation of surface micro/nano structures. Due to the high laser resolution on the order of micrometers, it shows a great advantage for the micro/nano manufacturing on surface fine structures. The surface micro/nano structures are distinct pits with hierarchical structures formed on the surfaces. Besides the laser surface treatment, other high-energy surface treatments also indicate the advantages of improving the surface properties of titanium alloys, such as micro arc oxidation, electron beam melting, etc. Combining the advantages of micro arc oxidation and the electrochemical polymerization of eugenol, the corrosion resistance of a titanium alloy was increased to 81.34% in the work by AlMashhadani et al. [70]. Zhang et al. [71] reviewed the application of electron beam melting on additive manufactured titanium alloys, and the porous structures in titanium alloys improved the biocompatibility further, as shown in Figure 11. The porous structure could provide porosity to encourage bone tissue growth and nutrient flow in order to achieve a better recovery effect. The porous size and structure can be adjusted via changing the electron beam energy and scanning speed.

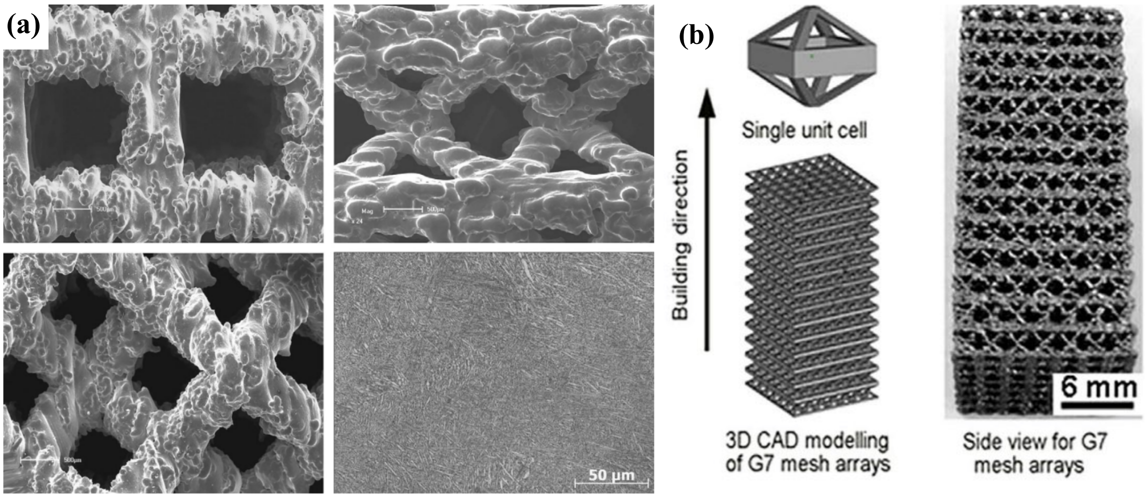

Figure 11. (**a**) The microstructures of Ti-6Al-4V porous samples with electron beam melting. (**b**) Porous structure model and side view of the Ti-24Nb-4Zr-8Sn component processed via electron beam melting [71]. (Reused with permission from ref. [71]. Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA).

Usually, the laser surface treatment is carried out in combination with other treatment methods, such as grinding, sandblasting and acidizing, nitriding, etc. However, the laser parameters for a possible choice are diverse, including laser energy, scanning speed, powder feeding speed, etc. The selection of these parameters directly affects the performance of the surface coatings; for instance, excessive laser power could introduce tensile residual stresses and cracks on the surface. Therefore, the selection of appropriate laser parameters is particularly important, especially in combination with other processing methods, which are still the focuses of future research and may be resolved via new methods of machine learning or big data processing.

2.6. Surface Mechanical Treatment of Titanium Alloys

In order to improve the mechanical properties of titanium alloy components, especially the fatigue properties, surface mechanical treatment is usually adopted to adjust the surface microstructure and the residual stress distribution, as it allows for excellent surface comprehensive mechanical properties to be obtained. Ren et al. [72] used ultrasonic rolling to modify the surface properties of Ti-6Al-4V, and, according to the simulation results, the best surface finishing was obtained while the static force was 1000 N and the amplitude was 8 μm, as shown in Figure 12. Du et al. [73] investigated the effect of cold rolling on the deformation mechanism of titanium alloys, and, with the increasing deformation level, the crystal orientation of matrix obviously changed. Pu et al. [74] utilized semi-solid stirring-assisted ultrasonic vibration to fabricate TiP/VW94 composites, and the tensile properties of the composites were improved because of the reinforcement of Ti particles. A strong interfacial bonding of the MnTi layer was formed due to the diffusion of Mn atoms. Wang et al. [75] used shot peening and the ultrasonic surface rolling process (USRP) method to improve the fretting fatigue performance of Ti-6AI-4V, which was ascribed to the lower surface roughness compared to that achieved using the shot peening process. In the work by Liu et al. [46], a new ultrasonic nano-crystal surface modification (UNSM) technique was adopted to strengthen the surfaces of titanium alloys. The surface hardness, residual compressive stress, and fatigue-related and tribological properties of the materials were improved.

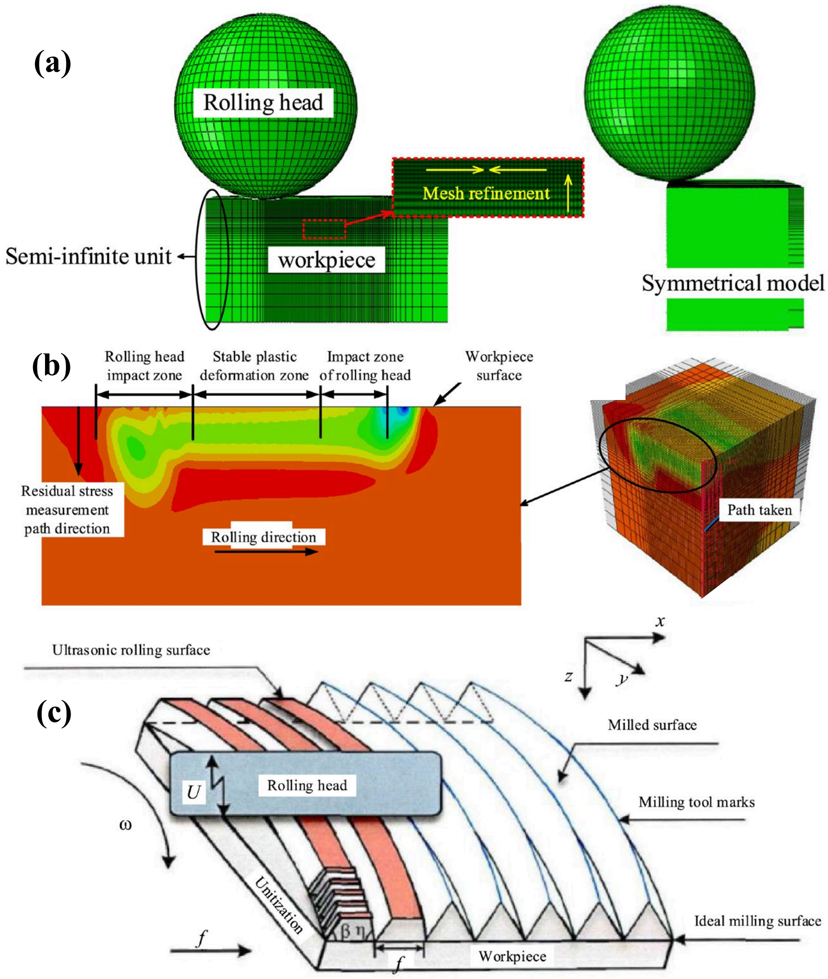

Figure 12. (**a**) Mesh division of a 3D finite element model; (**b**) residual stress distribution (left) and junction path (right) after ultrasonic rolling; the green area indicates the stable residual compressive stress layer near the surface of the processed workpiece; (**c**) schematic diagram of ultrasonic rolling [72]. (Reused with permission from ref. [72]. Copyright 2022, Elsevier).

Similarly, ultrasonic surface rolling treatment was utilized to modify the rolling contact fatigue (RCF) behavior of 17Cr2Ni2MoVNb steel in Zhang et al.'s work [76]. The material, under 1000 N, exhibited a maximum mean RCF life of 3.71×10^6 cycles, which was ascribed to the grain refinement and the residual compressive stress. Klimenov et al. [77] carried out surface modification on VT1-0 (α-phase) and VT6 (α + β phase) titanium alloys using ultrasonic treatment. The microhardness was enhanced with the increase in the initial surface roughness, which was ascribed to the surface nanocrystals as 100 nm for VT1-0 and 50 nm for VT6. The roughness of the surface of VT1-0 changed from Rz = 5 µm to 100 µm, causing by the successively located ridges and roots of a certain height at a constant pitch, which of VT6 under same modes showed an obviously lower surface roughness as compared to samples of VT1-0. As a result, with the decrease in the plasticity, the metal deforms less, the build-up reduces, vibrations reduce, and the cleanliness level of the treated surface increases. Li et al. [78] optimized the diffusion bonding of dissimilar TC17/TC4 titanium alloys using surface nano-crystallization (SN) treatment. Moreover, the shear strength of the SN-TC17/TC4 bond increased from 275 MPa at 973 K to 634 MPa at 1013 K due to the acceleration of void shrinkage. A schematic illustration of the evolution mechanism is shown in Figure 13. Comparing Figure 13a–c to Figure 13d–f, the surface SN layer on the SN-TC17 side enhances the grain/phase boundary diffusion and volume diffusion processes and the plastic flow effect, which accelerates the void shrinkage of the SN-TC17/TC4 bond and promotes the shear strength of the SN-TC17/TC4 bond.

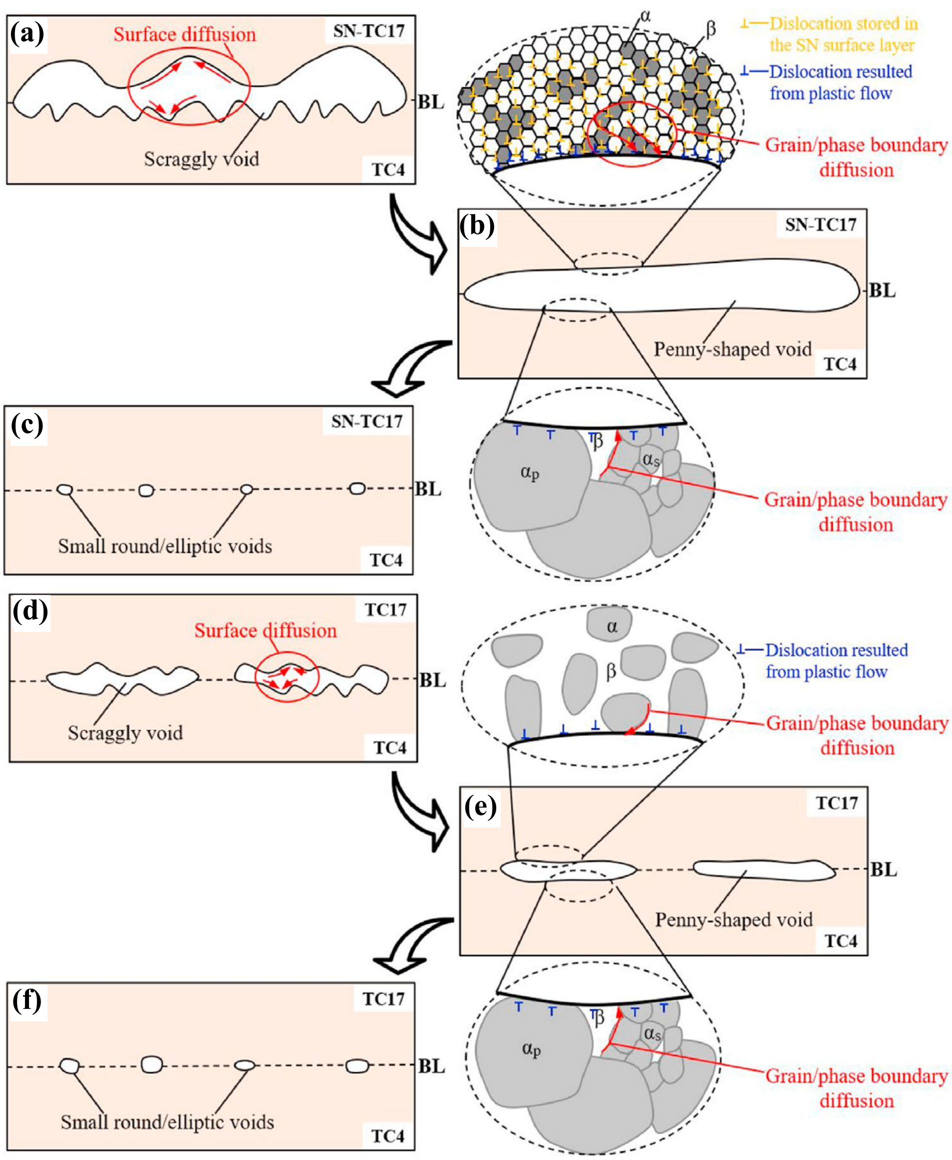

Figure 13. Evolution mechanism of voids in the bonding interface of SN-TC17/TC4 and TC17/TC4 bond: (**a**,**d**) are scraggly voids, (**b**,**e**) are penny-shaped voids, and (**c**,**f**) are round/elliptic voids [78]. (Reused with permission from ref. [78]. Copyright 2022, Elsevier).

The surface mechanical treatment of titanium alloys is usually related to fatigue properties. The relation between them is the microstructure, and the main mechanism is ascribed to the surface's micro-/nanostructure and residual compressive stress. The residual stress distribution was found to be more uniform and the static force and amplitude were increased after surface mechanical treatment. Regarding the mechanical treatment methods, shot peening is the most conventional method, but it also has some shortcomings, such as the high surface roughness and increased surface defects under severe plastic deformation. Therefore, the conventional shot-peening method combined with other treatment methods is a more reasonable choice. According to the discussion in this section, the surface microstructures and defects of titanium alloys can be improved by microstructure optimization and compressive residual stress introduced by surface mechanical treatment, which are ascribed to the surface nanolayer and the compressive residual stress distribution. Surface treatments of titanium alloys have been used in many different fields [79,80]. Each method has its own advantages and characteristics, as well as its own suitable materials and application range. Thus, researchers can choose the appropriate surface treatment method according to the relevant characteristics.

3. Conclusions and Prospects

Regarding the influence of surface treatments on titanium alloys, three aspects should be noted: (1) the effect of surface treatment on the microstructure and mechanical properties of titanium alloys; (2) the influence of surface treatment on the friction and wear properties of titanium alloys; and (3) the improvement of the biocompatibility of titanium alloys after surface treatment. Based on the above three aspects, the progress of research into surface treatment technologies for titanium alloys was reviewed in this work, and many new single methods and more hybrid methods have been introduced.

The single methods of surface treatment on titanium alloys were adopted from the mechanical surface treatments, the electrochemical/chemical surface treatments, etc. The representative single-treatment methods of shot peening, laser shot peening, nitriding, nitrocarburizing, etc., were summarized. Although some ne w and better results have been obtained via a single surface treatment, limitations still exist. Shot peening is the most conventional method of the mechanical treatment, but high surface roughness and increased surface defects are formed under severe plastic deformation. Nitrocarburizing provides a pathway towards an advanced material with both high strength and good plasticity, but the influence of the hardening layer on surface properties is still a difficult point that needs to be investigated further. Now, the laser surface treatment is a very popular method and some great results have obtained. The laser parameters for a possible choice are diverse, including laser energy, scanning speed, powder feeding speed, etc.; however, excessive laser power could introduce tensile residual stresses and cracks on the surface.

Therefore, the single-surface-treatment method combined with other treatment methods (hybrid surface treatment) is a more reasonable choice. The hybrid surface treatment methods were developed by focusing on combining two or more methods, for example, combining the mechanical surface treatments and the electrochemical/chemical surface treatments; the surface treatment coatings, etc. The representative hybrid surface treatment methods, like the shot peening combined with deposition, the laser boriding combined with composite alloying, etc., were also discussed. Laser surface treatment is carried out combined with other treatment methods, like grinding, sandblasting and acidizing, nitriding, etc. Hybrid surface treatments can bring many advantages, but the demands of its equipment are more complex, and the parameters become so as well; thus, more time is needed in order to find a reasonable process with an optimized set of parameters. With the development of surface treatment technologies for titanium alloys, hybrid surface treatments will be carried out more often in the future.

When a combination of two or more surface modification technologies is used on a titanium alloy, it can lead to better surface functions and achieve the comprehensive performance of "1 + 1 > 2". Moreover, the selection of appropriate parameters is particularly important, especially in combination with other processing methods. These are still research focuses for the future and may be resolved via new methods of machine learning or big data processing.

Author Contributions: B.X.: conceptualization, experiment, analysis, methodology, writing—original draft. K.G.: conceptualization, resources, supervision, writing—review and editing. 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: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Lu, W.; Zhang, D.; Zhang, X.; Wu, R.; Sakata, T.; Mori, H. Microstructural characterization of TiB in in situ synthesized titanium matrix composites prepared by common casting technique. *J. Alloys Compd.* **2001**, *327*, 240–247. [CrossRef]
2. Panigrahi, A.; Bönisch, M.; Waitz, T.; Schafler, E.; Calin, M.; Eckert, J.; Skrotzki, W.; Zehetbauer, M. Phase transformations and mechanical properties of biocompatible Ti–16.1Nb processed by severe plastic deformation. *J. Alloys Compd.* **2015**, *628*, 434–441. [CrossRef]
3. Attar, H.; Prashanth, K.G.; Chaubey, A.K.; Calin, M.; Zhang, L.C.; Scudino, S.; Eckert, J. Comparison of wear properties of commercially pure titanium prepared by selective laser melting and casting processes. *Mater. Lett.* **2015**, *142*, 38–41. [CrossRef]
4. Haghighi, S.E.; Lu, H.B.; Jian, G.Y.; Cao, G.H.; Habibi, D.; Zhang, L.C. Effect of α'' martensite on the microstructure and mechanical properties of beta-type Ti–Fe–Ta alloys. *Mater. Des.* **2015**, *76*, 47–54. [CrossRef]
5. Calin, M.; Zhang, L.C.; Eckert, J. Tailoring of microstructure and mechanical properties of a Ti-based bulk metallic glass-forming alloy. *Scr. Mater.* **2007**, *57*, 1101–1104. [CrossRef]
6. De los Rios, E.R.; Walley, A.; Milan, M.T.; Hammersley, G. Fatigue crack initiation and propagation on shot-peened surfaces in A316 stainless steel. *Int. J. Fatigue* **1995**, *17*, 493–499. [CrossRef]
7. Torres, M.A.S.; Voorwald, H.J.C. An evaluation of shot peening, residual stress and stress relaxation on the fatigue life of AISI 4340 steel. *Int. J. Fatigue* **2002**, *24*, 877–886. [CrossRef]
8. Kobayashi, M.; Matsui, T.; Murakami, Y. Mechanism of creation of compressive residual stress by shot peening. *Int. J. Fatigue* **1998**, *20*, 351–357. [CrossRef]
9. Fu, Y.; Loh, N.L.; Batchelor, A.W.; Liu, D.; Zhu, X.; He, J.; Xu, K. Improvement in fretting wear and fatigue resistance of Ti_6Al_4V by application of several surface treatments and coatings. *Surf. Coat. Technol.* **1998**, *106*, 193–197. [CrossRef]
10. Nalla, R.K.; Altenberger, I.; Noster, U.; Liu, G.Y.; Scholtes, B.; Ritchie, R.O. On the influence of mechanical surface treatments—Deep rolling and laser shock peening—On the fatigue behavior of Ti_6Al_4V at ambient and elevated temperatures. *Mater. Sci. Eng. A* **2003**, *355*, 216–230. [CrossRef]
11. Golden, P.J.; Hutson, A.; Sundaram, V.; Arps, J.H. Effect of surface treatments on fretting fatigue of Ti_6Al_4V. *Int. J. Fatigue* **2007**, *29*, 1302–1310. [CrossRef]
12. Liu, C.; Bi, Q.; Matthews, A. Tribological and electrochemical performance of PVD TiN coatings on the femoral head of Ti_6Al_4V artificial hip joints. *Surf. Coat. Technol.* **2003**, *163–164*, 597–604. [CrossRef]
13. Warren, J.; Hsiung, L.M.; Wadley, H.N.G. High temperature deformation behavior of physical vapor deposited Ti_6Al_4V. *Acta Metall. Mater.* **1995**, *43*, 2773–2787. [CrossRef]
14. Perry, S.S.; Ager, J.W., III; Somorjai, G.A.; McClelland, R.J.; Drory, M.D. Interface characterization of chemically vapor deposited diamond on titanium and Ti-6Al-4V. *J. Appl. Phys.* **1993**, *74*, 7542–7550. [CrossRef]
15. Baek, S.H.; Mihec, D.F.; Metson, J.B. The Deposition of Diamond Films by Combustion Assisted CVD on Ti and Ti_6Al_4V. *Chem. Vap. Depos.* **2002**, *8*, 29–34. [CrossRef]
16. Tsipas, S.A.; Vázquez-Alcázar, M.R.; Navas, E.M.R.; Gordo, E. Boride coatings obtained by pack cementation deposited on powder metallurgy and wrought Ti and Ti_6Al_4V. *Surf. Coat. Technol.* **2010**, *205*, 2340–2347. [CrossRef]
17. Çelikkan, H.; Öztürk, M.K.; Aydin, H.; Aksu, M.L. Boriding titanium alloys at lower temperatures using electrochemical methods. *Thin Solid Films* **2007**, *515*, 5348–5352. [CrossRef]
18. Sanders, A.P.; Tikekar, N.; Lee, C.; Chandran, K.S.R. Surface Hardening of Titanium Articles with Titanium Boride Layers and its Effects on Substrate Shape and Surface Texture. *J. Manuf. Sci. Eng.* **2009**, *131*, 031001. [CrossRef]
19. Wang, Z.M.; Ezugwu, E.O. Performance of PVD-Coated Carbide Tools When Machining Ti_6Al_4V©. *Tribol. Trans.* **1997**, *40*, 81–86. [CrossRef]
20. Senthil Selvan, J.; Subramanian, K.; Nath, A.K.; Kumar, H.; Ramachandra, C.; Ravindranathan, S.P. Laser boronising of Ti_6Al_4V as a result of laser alloying with pre-placed BN. *Mater. Sci. Eng. A* **1999**, *260*, 178–187. [CrossRef]
21. Wilson, A.D.; Leyland, A.; Matthews, A. A comparative study of the influence of plasma treatments, PVD coatings and ion implantation on the tribological performance of Ti_6Al_4V. *Surf. Coat. Technol.* **1999**, *114*, 70–80. [CrossRef]
22. Hutchings, R.; Oliver, W.C. A study of the improved wear performance of nitrogen-implanted Ti_6Al_4V. *Wear* **1983**, *92*, 143–153. [CrossRef]
23. Vreeling, J.A.; Ocelík, V.; De Hosson, J.T.M. Ti_6Al_4V strengthened by laser melt injection of WCp particles. *Acta Mater.* **2002**, *50*, 4913–4924. [CrossRef]
24. Man, H.C.; Zhao, N.Q.; Cui, Z.D. Surface morphology of a laser surface nitrided and etched Ti_6Al_4V alloy. *Surf. Coat. Technol.* **2005**, *192*, 341–346. [CrossRef]

25. Kloosterman, A.B.; Kooi, B.J.; De Hosson, J.Th.M. Electron microscopy of reaction layers between SiC and Ti_6Al_4V after laser embedding. *Acta Mater.* **1998**, *46*, 6205–6217. [CrossRef]
26. Lee, H.; Mall, S. Stress relaxation behavior of shot-peened Ti_6Al_4V under fretting fatigue at elevated temperature. *Mater. Sci. Eng. A* **2004**, *366*, 412–420. [CrossRef]
27. John, R.; Buchanan, D.J.; Jha, S.K.; Larsen, J.M. Stability of shot-peen residual stresses in an α+β titanium alloy. *Scr. Mater.* **2009**, *61*, 343–346. [CrossRef]
28. Liu, K.K.; Hill, M.R. The effects of laser peening and shot peening on fretting fatigue in Ti_6Al_4V coupons. *Tribol. Int.* **2009**, *42*, 1250–1262. [CrossRef]
29. Wang, G.; Wang, S.; Yang, X.; Yu, X.; Wen, D.; Chang, Z.; Zhang, M. Fretting wear and mechanical properties of surface-nanostructural titanium alloy bone plate. *Surf. Coat. Technol.* **2021**, *405*, 126512. [CrossRef]
30. Tan, T.; Zhao, Q.; Kuwae, H.; Ueno, T.; Chen, P.; Tsutsumi, Y.; Mizuno, J.; Hanawa, T.; Wakabayashi, N. Surface properties and biocompatibility of sandblasted and acid-etched titanium–zirconium binary alloys with various compositions. *Dent. Mater. J.* **2022**, *41*, 266–272. [CrossRef]
31. Liu, P.; Hao, Y.; Zhao, Y.; Yuan, Z.; Ding, Y.; Cai, K. Surface modification of titanium substrates for enhanced osteogenetic and antibacterial properties. *Colloids Surf. B Biointerfaces* **2017**, *160*, 110–116. [CrossRef] [PubMed]
32. Chae, K.; Jang, W.Y.; Park, K.; Lee, J.; Kim, H.; Lee, K.; Lee, C.K.; Lee, Y.; Lee, S.H.; Seo, J. Antibacterial infection and immune-evasive coating for orthopedic implants. *Sci. Adv.* **2020**, *6*, eabb0025. [CrossRef] [PubMed]
33. Bai, H.; Zhong, L.; Kang, L.; Liu, J.; Zhuang, W.; Lv, Z.; Xu, Y. A review on wear-resistant coating with high hardness and high toughness on the surface of titanium alloy. *J. Alloys Compd.* **2021**, *882*, 160645. [CrossRef]
34. Ren, B.; Wan, Y.; Liu, C.; Wang, H.; Yu, M.; Zhang, X.; Huang, Y. Improved osseointegration of 3D printed Ti_6Al_4V implant with a hierarchical micro/nano surface topography: An in vitro and in vivo study. *Mater. Sci. Eng. C* **2021**, *118*, 111505. [CrossRef] [PubMed]
35. Peng, R.; Zhang, P.; Tian, Z.; Zhu, D.; Chen, C.; Yin, B.; Hua, X. Effect of textured DLC coatings on tribological properties of titanium alloy under grease lubrication. *Mater. Res. Express* **2020**, *7*, 066408. [CrossRef]
36. Todea, M.; Vulpoi, A.; Popa, C.; Berce, P.; Simon, S. Effect of different surface treatments on bioactivity of porous titanium implants. *J. Mater. Sci. Technol.* **2019**, *35*, 418–426. [CrossRef]
37. Zhang, L.-C.; Chen, L.-Y.; Wang, L. Surface Modification of Titanium and Titanium Alloys: Technologies, Developments, and Future Interests. *Adv. Eng. Mater.* **2020**, *22*, 1901258. [CrossRef]
38. Cui, W.; Niu, F.; Tan, Y.; Qin, G. Microstructure and tribocorrosion performance of nanocrystalline TiN graded coating on biomedical titanium alloy. *Trans. Nonferrous Met. Soc. China* **2019**, *29*, 1026–1035. [CrossRef]
39. Takesue, S.; Kikuchi, S.; Misaka, Y.; Morita, T.; Komotori, J. Rapid nitriding mechanism of titanium alloy by gas blow induction heating. *Surf. Coat. Technol.* **2020**, *399*, 126160. [CrossRef]
40. Zhang, Y.S.; Zhao, Y.H.; Zhang, W.; Lu, J.W.; Hu, J.J.; Huo, W.T.; Zhang, P.X. Core-shell structured titanium-nitrogen alloys with high strength, high thermal stability and good plasticity. *Sci. Rep.* **2017**, *7*, 40039. [CrossRef]
41. Li, J.; Pang, X.; Fan, A.; Zhang, H. Friction and wear behaviors of Ti/Cu/N coatings on titanium alloy surface by DC magnetron sputtering. *J. Wuhan Univ. Technol. Mater Sci. Ed.* **2017**, *32*, 140–146. [CrossRef]
42. Takesue, S.; Kikuchi, S.; Akebono, H.; Morita, T.; Komotori, J. Characterization of surface layer formed by gas blow induction heating nitriding at different temperatures and its effect on the fatigue properties of titanium alloy. *Results Mater.* **2020**, *5*, 100071. [CrossRef]
43. Seo, D.M.; Hwang, T.W.; Moon, Y.H. Carbonitriding of Ti_6Al_4V alloy via laser irradiation of pure graphite powder in nitrogen environment. *Surf. Coat. Technol.* **2019**, *363*, 244–254. [CrossRef]
44. Zammit, A.; Attard, M.; Subramaniyan, P.; Levin, S.; Wagner, L.; Cooper, J.; Espitalier, L.; Cassar, G. Enhancing surface integrity of titanium alloy through hybrid surface modification (HSM) treatments. *Mater. Chem. Phys.* **2022**, *279*, 125768. [CrossRef]
45. Zhang, M.-X.; Miao, S.-M.; Shi, Y.-N. A Novel Surface Treatment Technique for Titanium Alloys. *JOM* **2020**, *72*, 4583–4593. [CrossRef]
46. Liu, R.; Yuan, S.; Lin, N.; Zeng, Q.; Wang, Z.; Wu, Y. Application of ultrasonic nanocrystal surface modification (UNSM) technique for surface strengthening of titanium and titanium alloys: A mini review. *J. Mater. Res. Technol.* **2021**, *11*, 351–377. [CrossRef]
47. Baris, N.M.; Golkovsky, M.G.; Tushinsky, L.I. SR-study of coatings obtained by complex electron-beam alloying of titanium alloys and steels. In Proceedings of the Proceedings KORUS 2000. The 4th Korea-Russia International Symposium on Science and Technology, Ulsan, Republic of Korea, 27 June–1 July 2000; Volume 3, pp. 407–410.
48. Casadei, F.; Pileggi, R.; Valle, R.; Matthews, A. Studies on a combined reactive plasma sprayed/arc deposited duplex coating for titanium alloys. *Surf. Coat. Technol.* **2006**, *201*, 1200–1206. [CrossRef]
49. Li, Y.; Zhou, Q.; Liu, M. Effect of novel surface treatment on corrosion behavior and mechanical properties of a titanium alloy. *Baosteel Technol. Res.* **2021**, *15*, 11–19. [CrossRef]
50. Tarbokov, V.A.; Pavlov, S.K.; Remnev, G.E.; Nochovnaya, N.A.; Eshkulov, U.É. Titanium Alloy Surface Complex Modification. *Metallurgist* **2019**, *62*, 1187–1193. [CrossRef]
51. Takesue, S.; Kikuchi, S.; Misaka, Y.; Morita, T.; Komotori, J. Combined Effect of Gas Blow Induction Heating Nitriding and Post-Treatment with Fine Particle Peening on Surface Properties and Wear Resistance of Titanium Alloy. *Mater. Trans.* **2021**, *62*, 1502–1509. [CrossRef]

52. Zammit, A.; Attard, M.; Subramaniyan, P.; Levin, S.; Wagner, L.; Cooper, J.; Espitalier, L.; Cassar, G. Investigations on the adhesion and fatigue characteristics of hybrid surface-treated titanium alloy. *Surf. Coat. Technol.* **2022**, *431*, 128002. [CrossRef]
53. Song, C.; Liu, M.; Deng, Z.-Q.; Niu, S.-P.; Deng, C.-M.; Liao, H.-L. A novel method for in-situ synthesized TiN coatings by plasma spray-physical vapor deposition. *Mater. Lett.* **2018**, *217*, 127–130. [CrossRef]
54. Hou, F.; Gorthy, R.; Mardon, I.; Tang, D.; Goode, C. Low voltage environmentally friendly plasma electrolytic oxidation process for titanium alloys. *Sci. Rep.* **2022**, *12*, 6037. [CrossRef]
55. Kazek-Kęsik, A.; Leśniak, K.; Zhidkov, I.S.; Korotin, D.M.; Kukharenko, A.I.; Cholakh, S.O.; Kalemba-Rec, I.; Suchanek, K.; Kurmaev, E.Z.; Simka, W. Influence of Alkali Treatment on Anodized Titanium Alloys in Wollastonite Suspension. *Metals* **2017**, *7*, 322. [CrossRef]
56. Rudawska, A.; Zaleski, K.; Miturska, I.; Skoczylas, A. Effect of the Application of Different Surface Treatment Methods on the Strength of Titanium Alloy Sheet Adhesive Lap Joints. *Materials* **2019**, *12*, 4173. [CrossRef] [PubMed]
57. Vlcak, P.; Fojt, J.; Koller, J.; Drahokoupil, J.; Smola, V. Surface pre-treatments of Ti-Nb-Zr-Ta beta titanium alloy: The effect of chemical, electrochemical and ion sputter etching on morphology, residual stress, corrosion stability and the MG-63 cell response. *Results Phys.* **2021**, *28*, 104613. [CrossRef]
58. Khodaei, M.; Amini, K.; Valanezhad, A.; Watanabe, I. Surface treatment of titanium dental implant with H_2O_2 solution. *Int. J. Miner. Metall. Mater.* **2020**, *27*, 1281–1286. [CrossRef]
59. Zhao, J.; Chen, D.; Hao, C.; Mi, W.; Zhou, L. The optimization and role of Ti surface doping in thermochromic VO_2 film. *Opt. Mater.* **2022**, *133*, 112960. [CrossRef]
60. Zhao, G.; Xia, L.; Zhong, B.; Wu, S.; Song, L.; Wen, G. Effect of alkali treatments on apatite formation of microarc-oxidized coating on titanium alloy surface. *Trans. Nonferrous Met. Soc. China* **2015**, *25*, 1151–1157. [CrossRef]
61. Luo, Q.; Yin, S.; Sun, X.; Tang, Y.; Feng, Z.; Dai, X. Density functional theory study on the adsorption properties of SO_2 gas on graphene, N, Ti, and N–Ti doped graphene. *Micro Nanostruct.* **2022**, *171*, 207401. [CrossRef]
62. Shirazi, H.A.; Chan, C.-W.; Lee, S. Elastic-plastic properties of titanium and its alloys modified by fibre laser surface nitriding for orthopaedic implant applications. *J. Mech. Behav. Biomed. Mater.* **2021**, *124*, 104802. [CrossRef]
63. Guo, C.; Zhang, M.; Hu, J. Fabrication of hierarchical structures on titanium alloy surfaces by nanosecond laser for wettability modification. *Opt. Laser Technol.* **2022**, *148*, 107728. [CrossRef]
64. Wang, Y.; Yu, Z.; Li, K.; Hu, J. Effects of surface properties of titanium alloys modified by grinding, sandblasting and acidizing and nanosecond laser on cell proliferation and cytoskeleton. *Appl. Surf. Sci.* **2020**, *501*, 144279. [CrossRef]
65. Pan, X.; Wang, X.; Tian, Z.; He, W.; Shi, X.; Chen, P.; Zhou, L. Effect of dynamic recrystallization on texture orientation and grain refinement of Ti6Al4V titanium alloy subjected to laser shock peening. *J. Alloys Compd.* **2021**, *850*, 156672. [CrossRef]
66. Yao, X.; Shi, Y.; Li, T.; Wensheng, L. Forming Characteristics and Analysis of Nitrided Layers During the Laser Nitriding Titanium Alloy. *Rare Met. Mater. Eng.* **2019**, *48*, 4060–4067.
67. Dong, B.; Guo, X.; Zhang, K.; Zhang, Y.; Li, Z.; Wang, W.; Cai, C. Combined effect of laser texturing and carburizing on the bonding strength of DLC coatings deposited on medical titanium alloy. *Surf. Coat. Technol.* **2022**, *429*, 127951. [CrossRef]
68. Han, J.; Zhang, G.; Chen, X.; Cai, Y.; Luo, Z.; Zhang, X.; Su, Y.; Tian, Y. High strength Ti alloy fabricated by directed energy deposition with in-situ Cu alloying. *J. Mater. Process. Technol.* **2022**, *310*, 117759. [CrossRef]
69. Pan, X.; He, W.; Cai, Z.; Wang, X.; Liu, P.; Luo, S.; Zhou, L. Investigations on femtosecond laser-induced surface modification and periodic micropatterning with anti-friction properties on Ti_6Al_4V titanium alloy. *Chin. J. Aeronaut.* **2022**, *35*, 521–537. [CrossRef]
70. Abdulkareem AlMashhadani, H.; Khadom, A.A.; Khadhim, M.M. Effect of Polyeugenol coating on surface treatment of grade 23 titanium alloy by micro arc technique for dental application. *Results Chem.* **2022**, *4*, 100555. [CrossRef]
71. Zhang, L.-C.; Liu, Y.; Li, S.; Hao, Y. Additive Manufacturing of Titanium Alloys by Electron Beam Melting: A Review. *Adv. Eng. Mater.* **2018**, *20*, 1700842. [CrossRef]
72. Ren, Z.; Li, Z.; Zhou, S.; Wang, Y.; Zhang, L.; Zhang, Z. Study on surface properties of Ti_6Al_4V titanium alloy by ultrasonic rolling. *Simul. Model. Pract. Theory* **2022**, *121*, 102643. [CrossRef]
73. Du, Z.; He, Q.; Chen, R.; Liu, F.; Zhang, J.; Yang, F.; Zhao, X.; Cui, X.; Cheng, J. Rolling reduction-dependent deformation mechanisms and tensile properties in a β titanium alloy. *J. Mater. Sci. Technol.* **2022**, *104*, 183–193. [CrossRef]
74. Pu, D.; Chen, X.; Ding, Y.; Sun, Y.; Feng, B.; Zheng, K.; Pan, F. Effect of Ti particles size on the microstructure and mechanical properties of TiP/VW94 composites. *Mater. Sci. Eng. A* **2022**, *858*, 144140. [CrossRef]
75. Wang, N.; Zhu, J.; Liu, B.; Zhang, X.; Zhang, J.; Tu, S. Influence of Ultrasonic Surface Rolling Process and Shot Peening on Fretting Fatigue Performance of Ti_6Al_4V. *Chin. J. Mech. Eng.* **2021**, *34*, 90. [CrossRef]
76. Zhang, Y.-L.; Lai, F.-Q.; Qu, S.-G.; Liu, H.-P.; Jia, D.-S.; Du, S.-F. Effect of ultrasonic surface rolling on microstructure and rolling contact fatigue behavior of 17Cr2Ni2MoVNb steel. *Surf. Coat. Technol.* **2019**, *366*, 321–330. [CrossRef]
77. Klimenov, V.A.; Vlasov, V.A.; Borozna, V.Y.; Klopotov, A.A. Ultrasonic Surface Treatment of Titanium Alloys. The Submicrocrystalline State. *IOP Conf. Ser. Mater. Sci. Eng.* **2015**, *91*, 012040. [CrossRef]
78. Li, L.; Sun, L.; Li, M. Diffusion bonding of dissimilar titanium alloys via surface nanocrystallization treatment. *J. Mater. Res. Technol.* **2022**, *17*, 1274–1288. [CrossRef]

79. Urtekin, L.; Aydin, Ş.; Sevim, A.L.I.; GÖK, K.; Uslan, İ. Experimental Determination of Biofilm and Mechanical Properties of Surfaces Obtained by CO_2 Laser Gas-Assisted Nitriding of Ti_6Al_4V Alloy. *Surf. Rev. Lett.* **2022**, *29*, 2250154. [CrossRef]
80. Urtekin, L.; Keleş, Ö. Investigation of Mechanical Properties of TiN-coated Ti_6Al_4V Alloy for Biomedical Applications. *J. Def. Sci.* **2019**, *18*, 91–108.