

Dental Implants Materials

Subjects: Dentistry, Oral Surgery & Medicine

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The development of dental implantology is based on the detailed study of the interaction of implants with the surrounding tissues and methods of osteogenesis stimulation around implants, which has been confirmed by the increasing number of scientific publications presenting the results of studies related to both the influence of the chemical composition of dental implant material as well as the method of its surface modification on the key operational characteristics of implants.

Keywords: dental implant ; Ti and its alloys ; stainless steels ; Zr and its alloys

1. Introduction

According to the World Health Organization (WHO), oral diseases are prevalent noncommunicable diseases that afflict almost half of the world's population, i.e., around 45% or 3.5 billion individuals of all ages [1][2]. Complete tooth loss, or adentia, is steadily increasing with a peak occurrence in older age groups. Currently, there are over 350 million cases worldwide, resulting in a global prevalence rate of almost 6.82% [1]. In Russia, partial tooth loss is estimated to affect between 40% and 75% of the population, corresponding to a range of 58 million to 108 million people. And, the number of patients with such problems will increase as the average age of the population rises [3]. In addition to tooth loss caused by accidents (trauma), dental decay and gum diseases are key factors contributing to teeth loss. Untreated caries in permanent teeth affect 2.3 billion individuals, while over 514 million children suffer from untreated deciduous teeth caries, and more than 1 billion people, which represent 19% of the world's population over 15 years of age, have periodontal disease [4].

Thus, the development of the dental implants market is driven by the high prevalence of oral diseases and the goal of improving people's quality of life. The worldwide market for dental implants was estimated at \$9.27 billion in 2022 and \$10.09 billion in 2023, with a forecasted compound annual growth rate (CAGR) of 8.95% to hit \$18.42 billion by 2030 [4]. The dental implants market is growing due to a rise in tooth loss cases, increasing demand for cosmetic dentistry, and advancements in dental implant technology [5].

The advancement of dental implantology is based on a detailed study of the interaction of implants with surrounding tissues and methods of stimulating osteogenesis around implants. This has been demonstrated by the increasing number of scientific articles presenting the results of studies on the influence of the chemical composition of the dental implant material and the method of its surface modification on the key characteristics of dental implants (**Figure 1**).

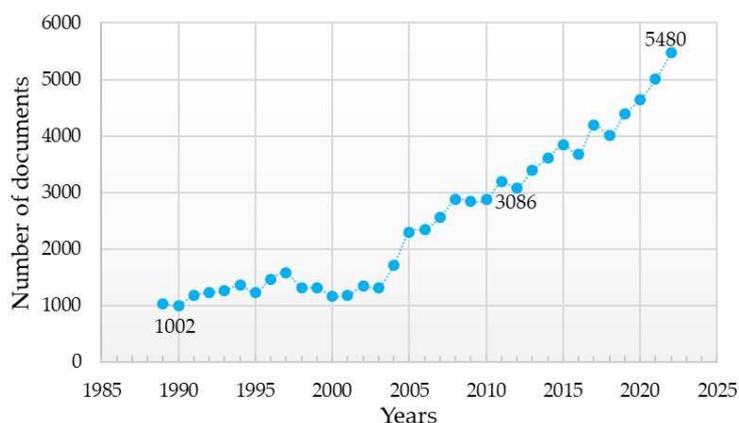


Figure 1. Analysis of search results for publications using the keywords “dental implant” from 1989, the year when the first patent for a titanium implant was registered, up to the present (according Scopus, ScienceDirect).

Figure 2 and **Figure 3** display the word cloud generated by keywords from the previously mentioned sample, limited to the period from 2014 to the present, where keywords related only to implant material and surface modification methods and properties were selected. According to the results presented, the main requirements for implants are to provide and/or enhance the following properties (these have been the focus of scientific research on the improvement of dental implants):

- Osseointegration, or the fusion of the implant surface with the bone [8][7][9][10];
- Bone regeneration, the process by which the body builds new bone tissue [11][12][13][14][15];

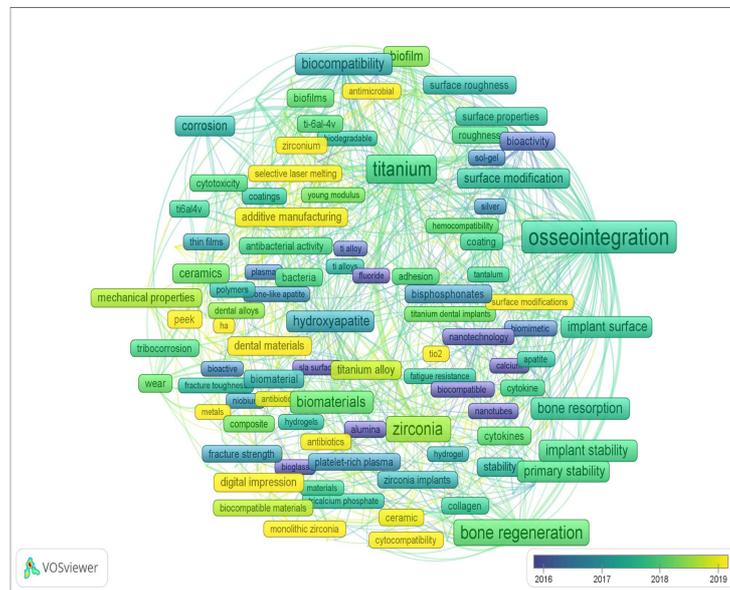


Figure 2. Overlay visualization of word cloud based on the keywords (dental implant) of publications from 2014 to present (according Scopus, ScienceDirect).

- Antibacterial ability, the ability of the implant to inhibit or slow down bacterial growth [16][17][18][19][20];
- Biocompatibility, the ability of the material to be integrated into the body without clinical complications and to induce the required cellular or tissue response [9][21][22][23][24][25].

Based on their biocompatibility, materials for dental implants can be divided into biotolerant, bioinert, and bioactive [26]. Biotolerant materials, such as stainless steel and cobalt–chromium alloys, induce osteogenesis in the bone to respond to the irritating effect of the implant in the tissue contact zone. In this case, a layer of soft fibrous tissue separates the bone from the implant composed of these materials. The application of bioinert materials, including alumina, zirconia, titanium, its alloys, and tantalum, leads to the development of contact osteogenesis given favorable mechanical conditions. This means that these materials directly bond with the bone tissue. Bone integration occurs because the surface of such materials is chemically inert to the surrounding tissues and fluids. Bioactive materials such as calcium phosphate ceramics, glass, and glass ceramics cause connective osteogenesis—the direct chemical bonding of the implant with the surrounding bone—due to the presence of free calcium and phosphate on the surface and of their interaction.

In addition, a number of scientific studies have been devoted to the influence of the above-mentioned factors on other properties of implants, for example:

- Bone resorption—the destruction (resorption, degradation) of bone tissue under the action of osteoclasts [27][28][29];
- Biomechanical stability—the ability of the implant to be reliably fixed in the bone tissue without clinical mobility [30][31][32];
- Osteoconductivity—the ability of the implant to provide bone tissue formation and growth on its surface (a special case of osteointegration) [33][34][35];

2. Dental Implant Materials

An artificial tooth (denture) is a complex construction (**Figure 5**) consisting of an implant (1), abutment (2) and crown (3). The implant itself is completely immersed deep into the bone, and the crown is located above the gingiva; the abutments connect them with each other, except in the use of one-piece implants, in which the intraosseous part and the abutment are immediately connected into a monolithic element (one-piece type of implants). However, this variant is mainly used for full jaw restorations, i.e., basal implantation (in one-stage implantation protocols involving immediate loading with a prosthesis).



Figure 5. Dental prosthesis: 1—implant, 2—abutment, 3—crown.

The implant material must meet several requirements ^[51]:

- To be strong enough to withstand chewing pressure (sometimes exceeding 100 kgf/cm^2) and not to destroy the bone with its weight;
- To be well machinable at the manufacturing stage in order to retain its shape throughout its entire service life;
- To not be destroyed (not corroded) by the action of the biological environment (saliva, blood, etc.);
- To not show toxic, allergenic, and carcinogenic effects on the body;
- To not provoke an increase in galvanic currents when interacting with metal structures installed in the patient's mouth.

The main materials for the production of dental implants, as mentioned before, are mainly metal alloys based on titanium, iron, and tantalum, as well as ceramics based on zirconium (**Figure 6**). At the same time, starting in the last twenty years, the number of studies in which the implants made of stainless steels are the objects of studies has considerably decreased (from 38% to 20%), and this has been connected with the presence of harmful impurities in the steel composition and the insufficient corrosion resistance and biocompatibility of these implants. At the same time, titanium and its alloys, during this period, have steadily occupied the leading positions (~50%), and today, they are the main materials for the production of commercialized dental implants.

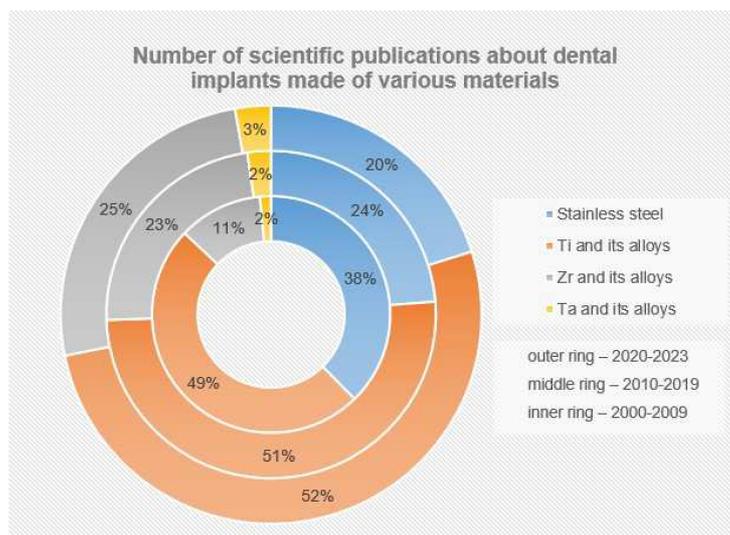


Figure 6. Number of scientific publications in the search results of publications for the keywords (dental implant*) from 2000 to the present (according to ScienceDirect). The number of publications (%) is presented relative to their total number for all groups of materials (SS+Ti+Zr+Ta).

2.1. Titanium and Its Alloys

The main materials for the production of dental implants are titanium and its alloys. For commercialized dental implants, the following grades of alloys are mainly used [52][53][54][55][56][57][58][59][60][61][62][63][64][65][66][67]:

- Grade 2 (cp-Ti) [53][54][55][56][57]—commercial pure titanium containing up to 0.3% iron;
- Grade 4 (cp-Ti) [57][58][59][60][61], which contains about 99% titanium and up to 0.5% iron;
- Grade 5 (Ti-6Al-4V alloy) [62][63][64][65][66][67], which is an alloy of titanium (88%) with aluminum (up to 6.75%) and vanadium (up to 4.5%);
- Roxolid[®], which is a high-strength alloy of titanium (about 85%) with zirconium (~13–17%), specially developed for use in dental implantology [68][69][70][71].

The chemical and mechanical properties of these alloys meet the requirements for materials used in dental implantation. They are characterized by high strength at low density, high elasticity (five times higher than the elasticity of bone [26]), and bioinertness [72], but not all titanium alloys are used in dentistry. However, with all these positive properties of titanium and its alloys, they are characterized by low resistance to shear and wear, especially under friction conditions [26].

At the same time, dental implants should be designed with a high coefficient of friction and a low modulus of elasticity to avoid excessive stress on the bone [73]. The modulus of elasticity of solid titanium alloys is 100–115 GPa, while the values for different types of bone are 0.5–20 GPa. This mechanical mismatch is the reason why healthy bones are underloaded and the “stress shielding” effect occurs [74]. The “stress shielding” effect leads to the healthy bone resorption and loosening of the implant, as a result of which the implant functioning period decreases.

This is why studies on obtaining “new”-generation titanium alloys with mechanical properties approaching the properties of bone tissue are conducted widely enough. All of them are aimed at the volumetric alloying of titanium alloys with β -stabilizers (Nb, Ta, Zr, and Mo) to obtain a single-phase β -alloy structure since β -Ti alloy has a lower modulus of elasticity and higher strength than α -Ti alloys and ($\alpha+\beta$)-Ti alloys [75]. In addition, the β -type titanium alloy has good technological properties (in particular, cold-pressure machinability), which reduces the cost of implant production [76].

Ti-6Al-4V alloy is 3.0–3.5 times stronger than commercially pure titanium and cheaper to produce [77], which makes it indispensable in the manufacture of thin, reliable implants with special compression threads that are placed in the dense basal regions of the jawbone [52]. However, vanadium and aluminum contained in the alloys have been shown [78][79] to have toxic effects on biological entities and can lead to long-term health problems, such as neurological diseases and Alzheimer’s disease [80][81][82][83], while aluminum and iron (although it is not a toxic element) lead to the formation of a connective tissue layer around the implant and to significant tissue contamination, which is a sign of the insufficient bioinertness of the metal. In addition, iron suppresses the growth of organic cultures. Also, the degree of tissue adhesion to the implants made of titanium alloys is somewhat worse than that to unalloyed titanium [84].

The introduction of Nb into the alloy composition, instead of toxic vanadium, improves the biointerface of alloys and leads to a significant increase in the wear resistance of alloys of the Ti-Al-Nb system in comparison with Ti-Al-V alloys, with comparable values in terms of fatigue strength and the service lives of products. Thus, it was shown in [85] that the wear resistance of Ti-21Al-29Nb and Ti-15Al-33Nb alloys was more than three times higher than that of Ti-6Al-4V. At the same time, at low- and multi-cycle fatigue tests on samples from both alloys, the following were observed: the nucleation of surface cracks, furrows in the zone of propagation of a stable fatigue crack, and equiaxed dimples in the zone of propagation of a fast-fatigue crack. The Ti-15Al-33Nb alloy exhibited ductile fracture morphology whereas the Ti-21Al-29Nb alloy tended to exhibit a more brittle fracture morphology.

The introduction of yttrium-stabilized zirconium oxide into the alloy of the Ti-Al-Nb system increases the Vickers microhardness and biocorrosion resistance of the alloy and improves the corrosion resistance of the alloy [86].

Moreover, Nb is non-toxic and has no harmful effect on the human body, which can be a result of its ability to form a protective oxide film on the implant surface like titanium. According to a study [87], Nb demonstrated good compatibility in contact with cells, providing mitochondrial activity and cell growth. Moreover, Ti-Nb alloys release fewer metal ions into the surrounding tissues compared to Ti-Al-V, Ti-Ni, and Ti-Mo alloys [88][89]. Ti-Nb alloys also have good mechanical strength (e.g., for Ti-42Nb alloy, the tensile strength is 683.17 ± 16.67 MPa and the compressive strength is 1330.74 ± 53.45 MPa [90]) and hardness (microhardness increases with increasing Nb content in the alloy—276 HV_{0.5} for Ti-13Nb and 287 HV_{0.5} for Ti-28Nb [91]) because Nb dissolves in the Ti crystal lattice, forming a solid substitution solution, which leads to the hardening of the solid solution β [92].

While, in binary Ti-Zr alloys, zirconium has almost no effect on β -phase stabilization, in multicomponent Ti alloys containing Nb or Ta, Zr acts as an effective β -stabilizer [76]. At the same time, Ti-Nb-Zr (TNZ) alloys have high strength (the tensile strengths of the alloys are in the range of 704–839 MPa) while remaining at the level of Ti-Nb alloys in terms of their low modulus of elasticity (in the range of 62–65 GPa) [76]. In addition, the new series of β -TNZ alloys have excellent cytocompatibility [76][93]. According to [93], due to its good mechanical properties ($E = 84.1$ GPa), high corrosion resistance, and lack of cytotoxicity toward MC3T3 and NHDF cells, this Ti-13Nb-13Zr alloy can be successfully used in implants, including in bone tissue engineering and dental products.

The additional alloying of a TNZ alloy with tantalum (TNZT alloy) leads to an increase in the corrosion resistance of the alloy in the environment of biological fluids (e.g., saliva, biofilm, and fluoride) while maintaining (with a decreasing trend) a relatively low modulus of elasticity ($E = 82$ GPa) [94]. The excellent biological and corrosion performance results are achieved mainly due to the oxide film (TiO₂, Nb₂O₅, ZrO₂, or Ta₂O₅) spontaneously formed on Ti and its alloys when exposed to atmospheric air [94]. The introduction of silicon into the composition of the TNZT alloy makes it possible to further reduce the elastic modulus (up to 50 GPa) [95]. At the same time, the Ti-Nb-Zr-Ta-Si alloy has a significant compatibility with bone tissue in comparison with the cp-Ti alloy, which is widely used in dental implants. Thus, in in vitro tests, in comparison with cp-Ti, Ti-Nb-Zr-Ta-Si alloy showed better adhesion, proliferation, and alkaline phosphatase (ALP) activity and promoted the expression of osteocalcin (OCN) mRNA in MG63 cells [95].

The addition of Mo not only stabilizes the β -phase of alloys but also increases the strength and maintains the ductility of Ti-Nb alloys, while Ti-Nb-Mo alloys are not prone to riveting [75]. This leads to a decrease in the modulus of elasticity, which is lower the more Mo is present in the alloy composition. Thus, the reduced elastic modulus (E_r measured via nanoindentation) decreases from 67.0 GPa for the Ti-26Nb-2Mo alloy to 54.5 GPa for the Ti-26Nb-8Mo alloy (with the lowest elastic modulus) [75]. In addition, the Ti-26Nb-8Mo alloy has good wear resistance and higher impact toughness than the cp-Ti alloy.

Despite the biocompatible composition, improved corrosion resistance, and low modulus of elasticity of complex-alloyed titanium alloys, serious aspects limiting the effectiveness of titanium alloys for biomedical applications are low tribocorrosion resistance in biological body environments and an inability to prevent bacterial infection in the early stages of recovery [96][97]. The latter can be addressed by alloying with antibacterial components such as Cu, Zn, Ag, and Ga [98].

In one study, although the addition of alloying elements Ga and/or Cu to the Ti-Nb matrix resulted in a slight increase in the elastic modulus to 73–78 GPa (for the base alloy Ti-45Nb, $E = 64$ GPa), the elastic modulus was still lower than that of the alloys used in clinical practice [99]. Among β -Ti-Nb-Ga alloys, increased wear resistance was noted for the Ti-45Nb-8Ga alloy [100], which is associated with increased microhardness (it increased by 32–44% with the addition of Ga and/or Cu, which the authors [99] attributed to the hardening of solid solutions). Also, the addition of Ga to Ti-45Nb leads to both improved corrosion resistance under mechanical loading as well as the increased strength of the alloy [100].

Another group of alloys used for the fabrication of dental implants, which have been clinically approved and already successfully commercialized, comprises Ti-Zr alloys [68][69][70]. For example, Ti-Zr alloys can compete in the fabrication of small-diameter dental implants. In these cases, cp-Ti is more prone to fracture (due to its relatively low compressive strength), and the use of Ti-Al-V alloy is undesirable due to the toxicity associated with the release of Al and V.

For binary Ti-Zr alloys (as mentioned earlier), Zr is a neutral component with respect to titanium and easily dissolves in both α - and β -solid substitution solutions of unlimited solubility of Ti(Zr) [101] (while strengthening it due to distortion of the crystal lattice of titanium when its atoms are replaced by zirconium atoms [102][103]) since it undergoes a similar allotropic transformation at a close phase transition temperature [104].

Ti-Zr alloys have a predominantly α -crystalline structure, which predetermines the enhanced mechanical properties and excellent electrochemical properties of these alloys [98][103]. Thus, the addition of 5 and 10 wt.% Zr to Ti allowed more than doubling the microhardness of the alloy (HV 416–434) compared to the microhardness of pure titanium cp-Ti (HV ~188), surpassing even the hardness of the Ti-6Al-4V alloy (HV 354) [105]. The tensile strength of binary Ti-Zr alloys also increases with increasing zirconium concentration in the alloy. In [106], it was shown that the tensile strength of Ti-15Zr alloy exceeds that of cp-Ti by about 10–15% (950 MPa vs. 860 MPa, approximately), which the authors attributed, first, to the hardening of the solid solution due to alloying, second, to the refinement of its grain size (1–2 μm in Ti-15Zr as opposed to 20–30 μm in cp-Ti), and third, to the riveting obtained during sample fabrication (strain hardening). However, Ti-Zr alloys have an increased modulus of elasticity, and the modulus of elasticity increases with increasing zirconium concentration in the alloy (for Ti-5Zr, Ti-10Zr, and Ti-15Zr alloys the values were ~86, ~95, and ~110 GPa, respectively [102]), but for Ti-Zr alloy with a Zr concentration of up to 10 wt.%, the modulus of elasticity was significantly lower than for the widely used Ti-6Al-4V alloy, which had a higher elastic modulus (~115 GPa [100]). At the same time, the minimum modulus of elasticity has an alloy containing about 7.5 wt.% Zr [102].

Also, Ti-Zr alloys demonstrate increased corrosion resistance in comparison with traditional titanium alloys, which can be associated with the formation of passivating ZrO_2 film on the implant surface. Thus, Zr for Ti is an anodic alloying component, which directly reduces its anodic activity [107], i.e., ZrO_2 is a more stable oxide than TiO_2 . And, although Ti^{4+} ions are more mobile than Zr^{4+} ions, which leads to a significant reduction in the amount of ZrO_2 oxide in the outer surface layer, the amount of the latter is proportional to the concentration of Zr in the alloy [105]. Higher corrosion protection for Ti-Zr alloys may also be facilitated by their increased hardness (and therefore wear resistance), which may prevent damage to the passivation film by mechanical stresses and ensure long-term rehabilitation success by reducing both the likelihood of corrosion in physiologic environments and the likelihood of impaired osseointegration [108]. In addition, it was shown in a study [105] that higher Zr concentrations resulted in enhanced albumin adsorption (albumin adsorption values for cp-Ti, Ti-6Al-4V, Ti-5Zr, and Ti-10Zr were 600, 650, 650, 750 mg/mL, respectively), suggesting, according to the authors, that there was no negative effect on initial cell adhesion.

Due to the sensitivity of mechanical properties to the structure of binary Ti-Zr alloys, it is possible to reduce the modulus of elasticity by applying strengthening heat treatment (accelerated cooling after heating above the $\beta \rightarrow \alpha$ transformation temperature) or strain hardening, which will change the distance between atoms, and this, in turn, can lead to a change in the bonding force between atoms and, as a result, the modulus of elasticity [102][109]. In addition, the use of additive technologies to create porous structures can also contribute to a decrease in the elastic modulus while maintaining the relatively high strength of the alloys. For this connection, additional studies are needed to reveal the influence of technologies for producing products from binary Ti-Zr alloys on their mechanical properties.

The additional alloying of Ti-Zr alloys with β -stabilizers (Nb, Mo and/or Ta) leads to a decrease in the elastic modulus [105][110][111] since the introduction of these components promotes the formation of β -phase in the structure, characterized by the lowest elastic modulus among all phases of titanium alloys [112]. Nb reduces the hardness of Ti-Zr alloy to a value close to the value of cp-Ti (~ 200 HV) [105], which is also associated with the appearance of a softer β -phase in the structure. The influence of zirconium concentration on the hardness of ternary Ti-Nb-Zr alloys is similar to that of binary Ti-Zr alloys; a study [105] showed the higher hardness of Ti-Nb-Zr alloys with higher Zr concentrations (in the range of zirconium concentrations of up to 10 wt.%).

However, as shown by studies, in complex alloys such as Ti-Zr-Nb-Mo, increasing the concentration of Zr from 34 to 40% (by replacing it with niobium while keeping the content of titanium and molybdenum constant) leads to a decrease in hardness (243 ± 4 , 2 HV, 238 ± 2.74 HV, and 237 ± 3.07 HV for Ti-34Zr-17Nb-1Mo, Ti-37Zr-14Nb-1Mo, and Ti-40Zr-11Nb-1Mo alloys, respectively) and alloy elastic modulus (75, 72, and 69.5 GPa for Ti-34Zr-17Nb-1Mo, Ti-37Zr-14Nb-1Mo, and Ti-40Zr-11Nb-1Mo alloys, respectively) [111] (in contrast to alloys with low zirconium content, i.e., up to 15 wt.%, for which hardness and elastic modulus increase with an increasing Zr concentration in the alloy [102]).

Biosafety evaluation tests (in accordance with the ISO 10993 series, [113]) of Ti-Zr alloyed with Nb and Ta [110] did not reveal any adverse (negative) effects either during extraction simulating normal use or under conditions of exaggerated extraction, which the authors attributed to the small number of released Ti ions. Thus, the concentrations of Ti in 0.9% NaCl + HCl solution when the samples from Ti-15Zr-4Nb, Ti-15Zr-4Nb-1Ta, and Ti-15Zr-4Nb-4Ta alloys were immersed in it were 0.4, 0.27, and 0.32 µg/mL, respectively. The authors of the study [110] substantiated such results via the presence of a passivating TiO₂ film formed on the Ti alloy surface and containing Nb₂O₅, ZrO₂, and Ta₂O₅ oxide films, which inhibited the yield of metal ions.

Another study [114] showed the prospects of the biomedical application of Ti-Zr alloys additionally alloyed with Fe. The Ti-6Zr-xFe alloy has an (α+β)-structure. With an increasing Fe content, from 4 to 7 wt.%, the volume fraction of α-phase decreases, the fraction of β-phase increases, and the grain size of the alloy as a whole decreases. This leads to an increase in microhardness (264–348 NV), the tensile strength (748–994 MPa) of cast Ti-6Zr-xFe alloys due to the hardening of the solid solution (due to iron alloying) and formation of ω-phase, and elastic modulus (90–94 GPa). At the same time, the alloys Ti-6Zr-4Fe and Ti-6Zr-5Fe (with the lowest Fe content) showed better corrosion resistance.

In each of the binary titanium alloys Ti-Ta and Ti-Mo, alloying with tantalum or molybdenum leads to higher strength and lower modulus of elasticity in the alloy compared to cp-Ti (similar to the effect of niobium) since Ta and Mo are also β-stabilizers. Thus, in a study, Ti-40Ta and Ti-50Ta alloys had higher tensile strength values compared to Ti-6Al-4V (786, 724, and 689 MPa, respectively), which were 14% and 8.9% higher than that of Ti-6Al-4V material [115], and the Ti-40Ta alloy with a biomimetic lamellar structure (obtained using sequential spark plasma sintering at 1200 °C followed by hot rolling at a strain rate of 60% and annealing) had a suitable combination of strength (tensile strength of 980 MPa, which was much higher than cp-Ti and comparable to Ti-6Al-4V) and low modulus of elasticity (80.4 GPa) [116]. It is worth noting that the strength and modulus of elasticity of Ti-Ta alloys are very sensitive to the Ta content; the dependence of these properties on the tantalum content in the binary Ti-Ta alloy has a complex character. Thus, the elastic modulus of the alloy first decreases almost linearly with an increasing Ta content and reaches a local minimum of 69 GPa at 30% Ta, then gradually increases and reaches 88 GPa at 50% Ta, and then gradually decreases and reaches a second local minimum of 67 GPa at 70% Ta. A further increase in Ta content leads to an increase in the elastic modulus, approaching the modulus of pure Ta [117]. The opposite dependence is observed for the tensile strength: at first, with an increasing Ta content, the strength increases, and the tensile strength reaches the first local maximum (595 MPa) at 30% Ta, then the strength slightly decreases to 530 MPa at 50% Ta. After that, it increases again and reaches the peak value of 690 MPa at 60% Ta; a further increase in Ta content slightly decreases the strength of the alloys [117]. The authors of [117] attribute these changes to the influence of tantalum concentration on the structure of binary Ti-Ta alloys (in their study, the alloys had a hexagonal (α') martensitic structure with a Ta content of up to 20%, orthorhombic (α'') martensitic structure at a Ta content from 30 to 50%, (α'' + β)-structure in the alloys with 60% Ta, and single-phase metastable β structure at a Ta content of more than 60%). In addition to tantalum concentration, the structure and, consequently, the properties of binary Ti-Ta alloys (by changing the phase composition and their ratio) are affected by the hardening heat treatment and plastic deformation (as confirmed by studies [117]).

In addition, Ti-Ta alloys have high biocompatibility and corrosion resistance. Thus, the results of a study [118] have confirmed that the corrosion resistance of Ti-Ta alloys with tantalum contents of 30, 40, 50 and 60 wt.% are not inferior to that of the Ti-6Al-7Nb alloy, and in fluorinated acidified saliva, even exceed it, which can be explained by the formation of Ta₂O₅ oxide film on the surface of a Ti-Ta alloy. At the same time, the authors of another study [119] state that a minimum of 40 wt.% Ta is recommended to achieve excellent corrosion properties in Ti-Ta alloys.

Tantalum also exhibits antibacterial activity against various pathogens such as *Staphylococcus aureus* and *Escherichia coli* [120][121], so further studies on the antibacterial activity of Ti-Ta alloys are needed.

As mentioned above, molybdenum acts as a strong β-stabilizer, which reduces the elastic modulus and increases the corrosion resistance of binary Ti-Mo alloys. Thus, Ti-Mo alloys with Mo content of up to 12% have lower elastic moduli than cp-Ti (138.56 GPa) [122]. However, the character of the influence of Mo concentration (in the concentration range from 3.2 to 12 at.%) on the elastic modulus of the alloy is identical to that of tantalum: the first local minimum corresponds to the Ti-3.2Mo alloy (83.8 GPa), the local maximum to Ti-6Mo (112.092 GPa), and the second local minimum to Ti-8Mo (82.98 GPa). It is worth noting that a significant increase in the elastic modulus between Ti-4.5Mo and Ti-6Mo alloys is observed when the Mo content increases up to 6 at.%, then its value falls sharply when the Mo content increases from 6 to 8 at.%, and when the Mo content changes from 8 to 12 at.%, only a slow increase is observed [122]. A further increase in the amount of molybdenum in binary alloys, as well as their additional alloying with zirconium, leads to an increase in the amount of β-phase in the alloy structure, which contributes to an even greater decrease in the elastic modulus while maintaining the increased strength of the alloy. In [123], it was shown that the ratios of α/β-phase (in %) for Ti-12Mo, Ti-

15Mo, Ti-12Mo-6Zr, and Ti-15Mo-6Zr alloys were 53.7/46.3, 50.61/49.39, 40.03/59.97, and 16.26/83.74, respectively. This also led to an increase in the hardness of the alloys and the elastic modulus of the alloys (**Figure 7**).

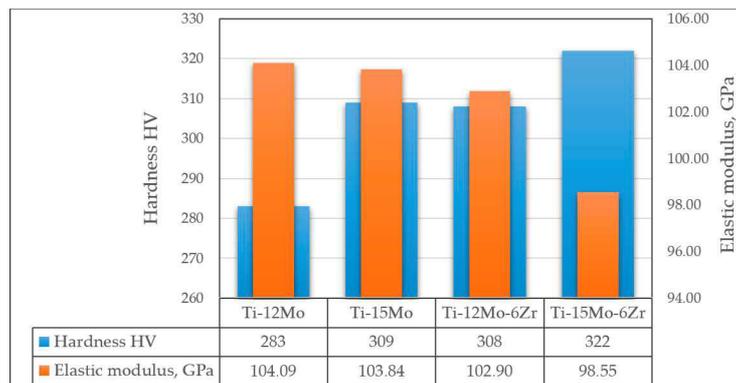


Figure 7. Hardness and elastic modulus of Ti-Mo and Ti-Mo-Zr alloys according to data.

The introduction of Fe into the ternary alloy of the Ti-Mo-Zr system reduces the elastic modulus of the alloy (from 105 GPa to 93 GPa with the addition of Fe from 1 to 3% [124]), while Ti-Mo-Zr-Fe alloys (containing from 1 to 4% Fe) are pseudo- β -alloys, i.e., the structure of the alloys contains up to 99% of the β -phase, the grain size of which decreases with increasing iron content [124].

Ti-Cu alloys are promising antibacterial biomaterials that have the potential to be tools against peri-implantitis and antibiotic resistance [125]. It was found that by varying the Cu concentration (1 to 10 wt.%) and aging temperature, the antibacterial properties of Ti-Cu alloys could be controlled. Thus, the best antibacterial properties were observed in the alloy with the maximum Cu content, Ti-10Cu, which was aged at 400 °C for 6 h [125], which may have been due to the high content of Ti₂Cu in the aged alloy and, as a consequence, a higher rate of release of Cu ions. It is worth noting that this alloy was the only material that showed an antibacterial effect after two hours of testing, while after six hours, bacteria were destroyed in all alloys with a Cu content of more than 5 wt.%.

Ti-Mg alloys have a low modulus of elasticity while maintaining the high specific strength and corrosion resistance inherent in cp-Ti (while the corrosion resistance and compressive modulus of Ti-Mg alloys decrease with increasing amounts of Mg) [126][127][128]. Moreover, Mg can dissolve in the modeled body fluids and contribute to the formation of a calcium phosphate layer; after the degradation of Mg, it is possible to obtain a porous titanium framework that promotes bone sprouting into the implant volume, i.e., the osseointegration and bioactivity of the implant are increased [128].

The introduction of Sr slows down the degradation rate of Ti-Mg alloys and increases their biocompatibility and bioactivity [129]. Sr promotes bone tissue regeneration and osteointegration at the interface (bone–implant), stimulates protein amalgamation, prevents osteoporosis, and suppresses bone resorption.

The alloys of the Ti-Mg-Sr system showed high mechanical properties in comparison with traditional alloys (cp-Ti, Ti-Al-V). Thus, the Ti-10Mg-20Sr alloy showed a low elastic modulus of 36 ± 7 GPa (measured by nanoindentation) with a hardness of 1.8 ± 0.8 GPa [129].

The addition of calcium to both titanium as well as noble metals (in particular, Pd, Pt) leads to an increase in the corrosion resistance of the binary alloys Ti-Ca, Ti-Pt, and Ti-Pd in acidic fluoride aqueous solutions (e.g., HF + NaF) adapted to different pH values (from 4.7 to 3.4) [130]. This was confirmed in a study [131], where it was shown that titanium alloys Ti-0.2Pd and Ti-0.3Mo-0.8Ni exhibited higher corrosion resistance than cp-Ti at fluoride concentrations below 0.002 M due to the accelerating effect of Pd and Ni on the cathodic process and the inhibiting effect of Mo on the anodic process.

In addition, the introduction of calcium and palladium into the composition of a titanium alloy contributes to the improvement of the osteointegration of the alloy. Thus, after 60 days of exposure to immersion in SBF solution with the addition of bovine serum albumin (0.8 g/l), precipitated CaP compounds (with Ca:P ratios from 1:0.7 to 1:4.4) were found on the surfaces of Ti-0.2Pd alloy samples [132].

Thus, alloying titanium alloys with β -stabilizers (Nb, Mo, Zr (for triple and more alloys), Fe, etc.) leads to a significant decrease in the elastic modulus and increase in the strength of alloys in comparison with traditional commercially available alloys (cp-Ti, Ti-6Al-4V), but it is not enough (the minimum elastic modulus of titanium alloys is 40–50 GPa, and that of bone is 4–30 GPa). The further reduction of Young's modulus is possible by creating porous structures with pore sizes of 100–500 μ m for better ingrowth of new bone tissue [127][133]. The prospectivity of this has been supported by

some studies. For example, it has been shown [127] that porous Ti fabricated using the high-pressure solid-state sintering (HPSSS) method has a high strength (~115 MPa), relatively low Young's modulus (~18 GPa), excellent ductility, and suitable pore sizes (50–300 μm), which make it attractive for load-bearing implant applications. Meanwhile, the strength of porous titanium can also be improved by alloying with Mo and Nb. Thus, porous alloy Ti-12.5Mo, with a porosity of 40–45%, and alloy Ti-25Nb, with a porosity of 39–48%, sintered at 1050 °C for 2 h, have excellent properties close to the properties of human cortical bone (Young's modulus is in the range of 5–18 GPa, with compressive strength in the range of 141–286 MPa), which correspond to the properties of bone [134]. In addition, in the study, the compressive strength and Young's modulus increased linearly with the decreasing porosity of the samples.

2.2. Zirconium and Its Alloys

In modern practice zirconium, and its alloys are used for dental implant manufacturing [135][136][137][138][139][140]. Comparing the values of the electrode potentials of titanium (-1.63 mV) and zirconium (-1.4 mV), it can be assumed that implants based on zirconium alloy are more preferable, which is due to the negative influence of the negative potential of the implantation material surface on the surrounding tissues [141]. The higher the negative value of the standard electrode potential of a metal is, the greater its solubility and reactivity will be [142].

The conducted analysis of the results of the above-mentioned search query has shown that two groups of zirconium-based alloys are used for dental implant manufacturing:

- Metal alloys of the Zr-Nb [143][144][145], Zr-Ti [103][146][147][148][149], Zr-Ti-Mo [135], Zr-Ti-Nb [150][151], Zr-Ti-Ag [146], Zr-Ta, and Zr-Ta-Ti [9] systems;
- Ceramic materials based on zirconium dioxide:
 - ZrO₂ [152][153][154][155][156][157];
 - ZrO₂ stabilized with cerium (Ce-TZP) [158][159];
 - ZrO₂ stabilized with yttrium (Y-TZP or YSZ) [160][161][162][163];
 - Ce-TZP/Al₂O₃ nanocomposite, which is a Ce-stabilized ZrO₂-based composite material reinforced with Al₂O₃ crystals or fibers (Al-TZP) [164][165][166][167].

Zirconium is a rather soft gray metal, but it has a lower modulus of elasticity (92 GPa), better corrosion resistance than Ti [168], and good biocompatibility and osteoinductivity [169]. Zr, similar to titanium, is allotropic. Therefore, metal alloys based on it (in particular, Zr-Nb) belong to the group of alloys with solid-solution hardening and differ from intermetallic alloys, i.e., those inclined to magnetization, which include titanium, based on the high characteristics of fatigue endurance that do not depend much on the metal structure [141].

In [145], the microstructure and mechanical properties of cast Zr-(0-24)Nb alloys were investigated. It was found that when Nb was introduced in small amounts (up to 6 wt.%), Zr-Nb alloys consisting mainly of α'-phase (containing less than 6 wt.% Nb) showed the highest strength (786–881 MPa), moderate ductility (6.5–3.7%), and relatively high Young's modulus (74 GPa) while maintaining low magnetic susceptibility. A further increase in niobium content led to a decrease in alloy strength (tensile strength of Zr-22Nb alloy was 605 MPa), which was associated with both the appearance of ω-phase as well as an increase in the amount of a less strong β-phase. It is worth noting that Young's modulus of Zr-Nb alloys at a niobium concentration of up to 24% (over the whole investigated range) was lower than the elastic modulus of the titanium alloy Ti-6Al-4V, with the minimum value of Young's modulus (48.4 GPa) being associated with alloy Zr-20Nb. Although the strength of this alloy was inferior to that of the Ti-6Al-4V alloy (687 MPa vs. 994 MPa), its value exceeded that of bone strength, and the magnetic susceptibility of the Zr-20Nb alloy was half that of the Ti-6Al-4V alloys, making it a preferred implant material for patients requiring MRI studies [145].

As mentioned above, zirconium and titanium have close atomic sizes and allotropic transformation temperatures, which allows these elements to form solid solutions of unlimited solubility. The properties of binary alloys Ti-xZr (where x is up to 90 at.%) have been discussed in detail above. Let us only add that metallic zirconium has excellent corrosion resistance in acid or alkali solutions but is subject to localized corrosion in media containing chloride or fluoride. The introduction of titanium into the alloy composition reduces the local corrosion of Zr-Ti alloys (while increasing the titanium content contributes to a decrease in the corrosion rates of the alloys), but their resistance to pitting corrosion is still inferior to that of cp-Ti [146]. Zr-20Ti and Zr-40Ti alloys exhibit good mechanical properties (the ultimate strength values are 1630 MPa

and 1884 Mpa, and the microhardness values are 330 HV and 340 HV, respectively) and good machinability in cold deformation (alloy deformations at fracture are 25.2% and 26.8%, respectively) [146].

Binary Zr-Ti alloys have a predominantly α -crystalline structure, and the introduction of molybdenum, which is a β -stabilizer, leads to a change in the alloy structure. With the gradual addition of Mo from 0 to 12.5 wt.%, the phase composition of the alloys changes as $\alpha \rightarrow \alpha + \beta \rightarrow \beta$, with the amount of β -phase increasing with the increasing Mo content [135]. The properties of Zr-Ti-Mo alloys fully meet the requirement of aligning with the mechanical properties of biomedical dental implants. Thus, the alloys Zr-25Ti-xMo (where x is from 0 to 12.5 wt.%) have a reduced compressive strength in the range of 1154.4 to 1310.8 MPa, yield strength of 673.2 to 996.0 MPa, and Young's modulus of 17.74 to 24.44 GPa, and the alloy Zr-25Ti-7.5Mo shows the best wear and corrosion resistance [135].

The introduction of Nb into the composition of Zr-Ti alloys also leads to the change of its structure to the β -type. Thus, the microstructure of the cast Zr-19Ti-21,4Nb alloy is represented by β -grains of 150–200 μm in size. The mechanical properties of this alloy in the deformed state correspond to the properties of the Ti-6Al-4V alloy (the tensile strength of the Zr-19Ti-21,4Nb alloy was 850–900 MPa, and the deformation of the alloy at fracture, characterizing plasticity, was 10.5%), but the modulus of elasticity is much closer to that of natural bone (37.6 GPa) [150]. The experiment with cell cultivation demonstrated the adequate adhesion of osteoblasts on the first day to both sr-Ti and Zr-Ti-Nb alloys, with subsequent proliferation on days 3 and 7. These data indicate the biocompatibility of Zr-19Ti-21,4Nb alloy and the absence of toxicity to cells [150].

The introduction of silver (6%) into Zr-Ti alloys leads to increased resistance to electrochemical corrosion (in particular, in artificial saliva containing fluorine). Moreover, the effect of Ag is stronger the more titanium is in the alloy composition since the joint action of titanium and silver promotes the formation of a thick, compact, and stable passive film [146]. At the same time, silver slightly changes the mechanical properties of Zr-xTi alloys. Thus, in a study, the introduction of 6% Ag increased the hardness of the Zr-20Ti alloy from HV 329 to HV 338, and the hardness of the Zr-40Ti alloy increased from HV 340 to HV 349 [146].

The Zr-30Ta and Zr-25Ta-5Ti alloys also showed improved biocompatibility and osteogenic activity in comparison with cp-Ti due to, among other things, favorable surface properties (increased surface hydrophilicity and roughness) [9]. Thus, the Zr-25Ta-5Ti alloy had the smallest contact angle ($\sim 30.6^\circ$) and the largest roughness value ($R_a = 34.8 \text{ nm}$) while, for the Zr-30Ta alloy, the values of the contact angle of wettability and roughness were 46.6° and 20.7 nm, respectively (for comparison, these characteristics for cp-Ti were 52° and 13.1 nm). The differences between the samples were statistically significant ($p < 0.01$). In addition, the Zr-30Ta and Zr-25Ta-5Ti alloys also induced the balanced expression of M1 and M2 macrophage phenotypes during the first 24 h. A Zr-25Ta-5Ti sample adsorbed three times more protein ($(147.4 \pm 13.26) \mu\text{g}$) compared to Zr-30Ta ($(32.1 \pm 4.57) \mu\text{g}$) and CP-Ti ($(32.4 \pm 3.7) \mu\text{g}$) samples.

Unlike metallic zirconia, ZrO_2 , zirconium dioxide, is an ultra-hard material; at the same time, it has a white color similar to that of the natural tooth root, which is favorable for restorations in the smile area [153], and it is biocompatible, does not provoke allergies, and is one of the most durable in service [141]. The zirconia surface is poorly adhered to by bacteria (40% less adhesion than metals) [170][171], and ceramic materials are less prone to plaque accumulation than metal substrates [167].

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