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RECENT TRENDS IN THE DEVELOPMENT OF Ti–Zr-BASED ALLOYS FOR BIOMEDICAL APPLICATIONS AND HYDROGENATED POWDER TECHNOLOGIES FOR THEIR MANUFACTURING

Alloys based on Ti, Zr, Nb and Ta are the main metal biomedical materials. The proper selection of compositions based on these elements provides the necessary biocompatibility and mechanical compatibility with bone and other tissues of a living organism, as well as high strength with sufficient corrosion resistance in acid and alkaline environments, which are the key criteria in the manufacture of medical implants. The advantages of producing biomedical alloys using powder technology, in comparison with conventional techniques (such as vacuum casting and hot deformation), are discussed. The use of hydrogen as a temporary alloying element in powder technologies of these metals, and the positive effect of hydrogen on reducing residual porosity in the formation of alloys with an enhanced complex of physical and mechanical properties, are considered.

Keywords: biocompatible materials, titanium, zirconium, Young's modulus, corrosion resistance

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1. Basic Requirements for Biocompatibility, Physical and Mechanical Properties of Metallic Materials for Medical Applications

There is evidence that as early as 4,000 years ago, people began using artificial materials to repair damaged tissues and organs of the human body [1]. In the early centuries, the Greeks and Egyptians implanted wood and animal bones in people. However, it was only in 1546 that a metallic material (gold plate) was first tested in experiments with animals to restore wolf teeth. Despite this [2], the field of science dealing with the development of materials for biomedical applications received due recognition only after the first seminar on biomaterials at Clemson University, South Carolina, in 1969 [2], and since then it has only increased in pace [3–5]. Biomaterials are artificial or natural materials used for making structures or implants to replace a lost or diseased biological structure to restore its shape and function (Fig. 1) [6]. The development of biomaterials with the required properties helps to improve the quality and increase the life expectancy of a living organism.

The main requirements for medical materials [7], which can be used for the manufacture of orthopaedic, dental, and cardiovascular implants, as well as medical devices and instruments, are high corrosion resistance and biological compatibility.

Biomedical materials should be absolutely non-toxic and not cause chemical, inflammatory or allergic reactions in a living organism. The possibility of using biomaterials depends largely on the reaction of the human body to the implant [8]. The biocompatibility of a material is determined by two main factors: the reaction of biological tissues caused by the material and the degradation of the material themselves in the body environment [1]. When implants are exposed to body tissues and fluids, several types of chemical reactions are possible between the host and the implant material, which determine the acceptability of these materials to humans. According to the biocompatible characteristics (Fig. 2), metallic materials can be divided into three main groups [9]: (i) chemical elements that are toxic to living organisms, which can interact with biological tissues rather actively (nickel, vanadium, copper, cobalt); (ii) chemical elements that are encapsulated in biological environments, covered with a passivation layer, and therefore are considered relatively inert (stainless steels, cobalt-chromium alloys, iron, aluminium, gold, *etc.*); (iii) completely biocompatible and inert elements that do not have any negative impact on a living organism (titanium, zirconium, niobium, tantalum, platinum).

Given the compliance of the properties of various alloys with the complex of the above biocompatibility requirements, the main metallic materials for biomedical use today are stainless steels, Co–Cr alloys, and Ti-based alloys of various alloying systems [10–13].

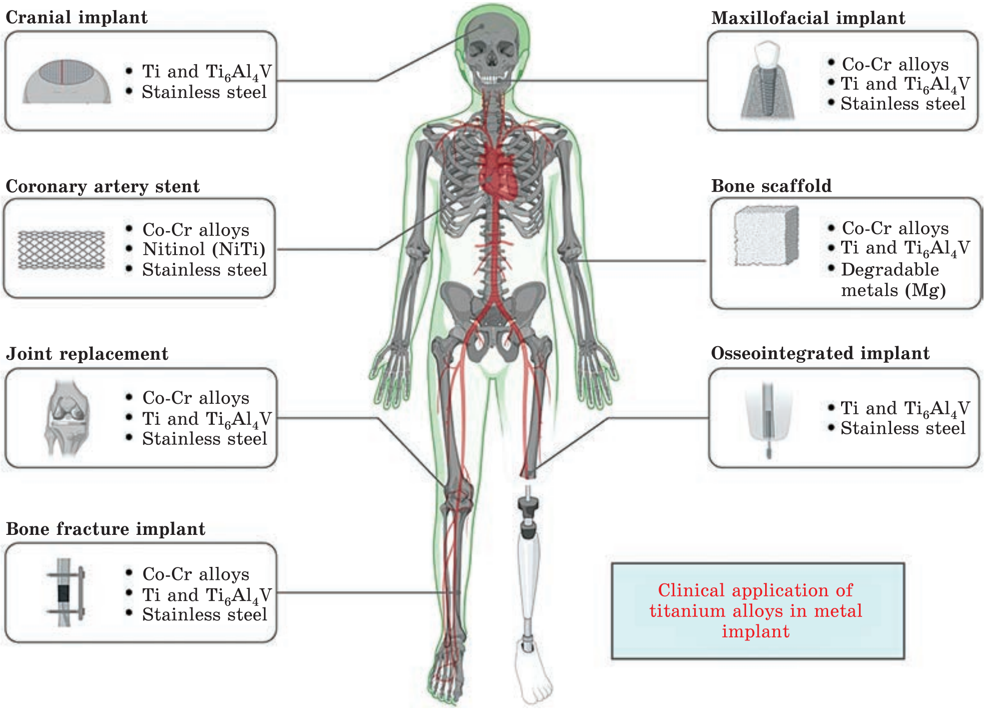

Fig. 1. Metal implant in the human body, highlighting the clinical applications of Ti alloys in cranial, maxillofacial, orthopaedic, and cardiovascular devices [6]

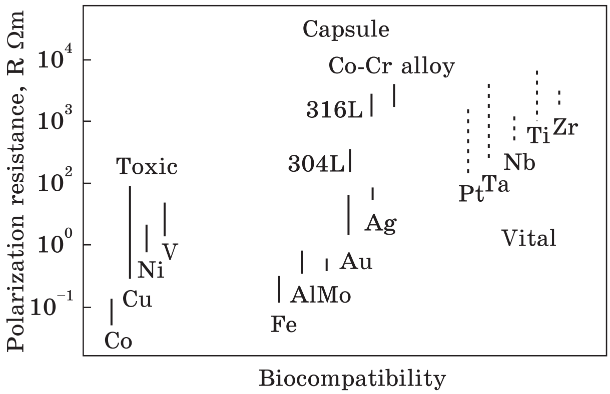

Fig. 2. Biocompatibility and polarization resistance of metallic materials [9]

Besides the biocompatibility characteristics, the key role in the manufacture of implants is played by the compliance of the physical and mechanical characteristics of the materials with certain criteria. For implant material, the main mechanical parameters are high strength, sufficient fatigue properties, hardness and ductility characteristics. Besides [2], an extremely important criterion is the mechanical compatibility of the implant material and bone tissue, *i.e.*, the correspondence of Young's modulus of the implant to the modulus of human bone (Fig. 3). The Young's modulus of the material attached to the bone should be close to the bone modulus, which is from 4 to 30 GPa, depending on the type of bone and

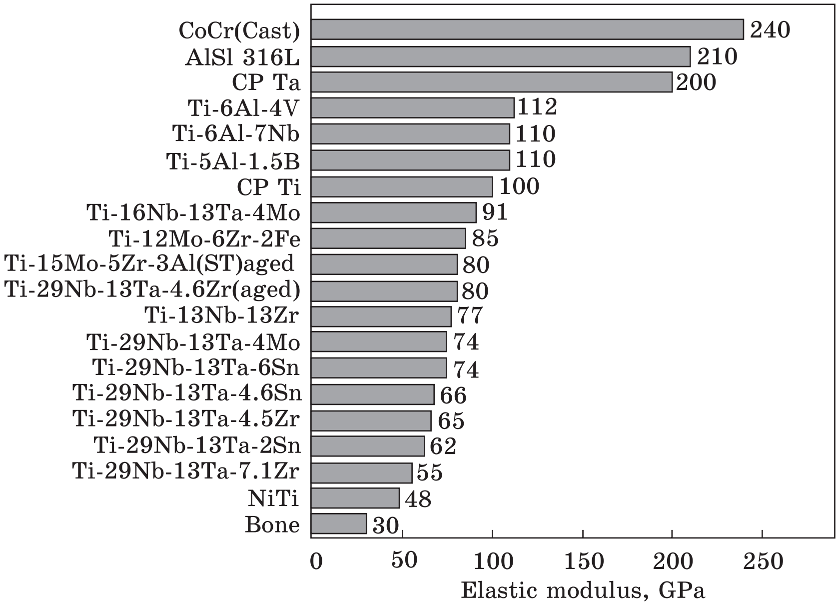

Fig. 3. Comparison of Young's moduli of biomedical alloys and human bone [2]

the direction of loading [14]. If the bone is replaced with a metal analogue with a significantly higher modulus of elasticity, this implant usually bears most of the mechanical stresses, protecting the parts of the skeleton around it from normal loads. This leads to resorption of the bone around the implant, and therefore to a weakening of the bond tissue between the implant and the bone. This biomechanical incompatibility ('stress shielding effect') leads to the death of bone cells [14]. Therefore, implants require materials with an excellent combination of high strength, fatigue strength, and low Young's modulus close to that of bone, to increase their service life [8].

Wear resistance and corrosion resistance are important properties of metal implant materials that determine their service life. The low resistance of metal products to wear and corrosion in a living body leads to the release of incompatible metal ions into the body from implants, which causes allergic and toxic reactions [15]. Low wear resistance also leads to loosening of implants, and wear fragments cause negative reactions in the tissue in which they deposit [16]. Therefore, the development of metallic materials with high corrosion and wear resistance is of primary importance for their long-term operation in biological environments. Besides, the state of the material surface is important, as its chemical composition, roughness, and topography play a significant role in the development of implant-biological tissue integration [17]. Controlled porosity and surface roughness of the implant contributes to its improved integration with biological tissues [17].

Due to the good compliance with the above requirements, stainless steels, Co–Cr alloys, and Ti-based alloys of various alloying systems are the main metallic materials for the manufacture of implants [10–13], although they have certain disadvantages.

For example, stainless steel 316L (Fe–18Cr–12Ni–2.5Mo–2Mn, wt.%) is widely used in medicine [18]. This is a molybdenum-containing austenitic stainless steel that is more resistant to general corrosion and pitting/crevice corrosion than the conventional chromium-nickel austenitic stainless steels such as Type 304 [19]. In addition to excellent corrosion resistance, this steel also has high strength (500–700 MPa) and good machinability [20]. However, stainless steels also have certain disadvantages: in particular, the proneness to cracking under the combined effect of tensile stresses and an aggressive environment enriched with Cl^- ions (which is typical for human body tissues). This causes an unexpected and instantaneous failure of the implant under the influence of stresses that are much lower than the theoretical strength of steel [21].

Alloys based on the Co–Cr system, in particular Co–Cr–Mo and Co–Cr–W ones, have enhanced mechanical properties, including strength, as well as high corrosion resistance and wear resistance [13, 22]. The martensitic transformation that occurs in these alloys under plastic deformation contributes to 'enhanced work hardening and high wear resistance' [22]. The high Cr content in Co–Cr alloys [23, 24] results in the formation of a thin surface oxide scale (Cr_2O_3) [24], which has even better corrosion resistance in the human body than 316L stainless steel. However, the prolonged presence of 316L stainless steel and Co–Cr-based alloy implants in the human body leads to the gradual development of corrosion and wear, with elements such as Ni, Co, and Cr being released from the implants into the adjacent tissues [25], which results in negative consequences. Nickel and cobalt can cause allergies, skin diseases, and have carcinogenic effects [26, 27]. Chromium can damage kidneys, liver and blood cells through oxidation reactions [28]. Besides, the negative features of 316L steel [20] and alloys based on the Co–Cr system are their high Young's moduli in the range of 190–240 GPa, which is about 10 times higher than that of human bones, which leads to mechanical incompatibility (the so-called 'stress shielding' effect) [29].

It is possible to avoid the above disadvantages by manufacturing implants from titanium alloys of various alloying systems, which are extremely attractive for biomedical use [9, 12], having high strength, sufficient corrosion resistance, excellent biocompatibility, high ability to contact with bone and other tissues and a reduced elastic modulus compared to stainless steels and Co–Cr alloys.

2. General Characteristics of Titanium-Based Biomedical Materials

Titanium has been used as a biomedical material since the 1950s [2, 12]. The surface of titanium is covered with a TiO_2 passivation film, which makes it extremely inert to acid and alkaline environments, as well as biological tissues. Commercially pure (unalloyed) titanium (CP-Ti) [2] with α-h.c.p. lattice is widely used for implant manufacturing, as it is an ideal material in terms of high biocompatibility (Fig. 2). However, its strength (345 MPa for Grade 2) and fatigue limit are insufficient, while its elastic modulus is significantly higher than the Young's modulus of bone, amounting to 105 GPa [30]. Later, two-phase α-h.c.p. + β-b.c.c. titanium alloys were widely used in medicine, mainly the Ti–6Al–4V alloy (wt.%) with significantly higher strength (820–950 MPa) and Young's modulus of 110 GPa, despite it contains toxic vanadium [2, 12, 31]. This alloy has well-balanced mechanical properties, and in order to better meet the requirements of biomedical use, the modification of Ti–6Al–4V ELI [32] (extra-low interstitial) is used for manufacturing implants, with a significantly reduced level of interstitial impurities (O, N, C, H). At the next stage, alloys with similar phase composition and mechanical properties were developed, in which toxic vanadium was substituted with safer elements: Ti–5Al–2.5Fe [33] and Ti–6Al–7Nb [32, 34]. The advantage of two-phase (α+β) alloys [35, 36] is the significant potential for changing their phase and structural states, which makes it possible to vary the complex of mechanical properties by heat treatment in a rather wide range. However, the Young's modulus of all two-phase (α+β) alloys is about 105–110 GPa, *i.e.*, it is close to the value for single-phase CP-Ti with α-h.c.p. lattice (Fig. 4), which is not the optimal choice for biomedical implants, since it does not solve the issue of mechanical compatibility of implants with bone tissue.

Given that the elastic modulus of the b.c.c. β-Ti phase (70–90 GPa [31]) is lower than that of the h.c.p. α-phase (105 GPa [31]), the logical solution for implant materials is to develop compositions enriched with alloying elements that increase the content of the β-phase in titanium alloys or provide the formation of the single β-phase state (Fig. 4). The high-temperature β-phase is stabilized at room temperature by adding a sufficiently high amount of β-stabilizers to titanium, such as molybdenum, niobium, tantalum, vanadium, iron, *etc.* [37]. Compositions based on the β-phase (Fig. 4) are the most promising not only in terms of reducing the Young's modulus, but also due to the possibility to adjust the complex of their mechanical properties by changing the chemical composition. Taking into account the criterion of biological compatibility (Fig. 2), Nb and Ta are recommended for stabilizing the β-phase [38]. These alloying elements are used most often, as they also provide high strength and reduced elastic modulus [39–43]. The absence of microgalvanic interphase effect in the

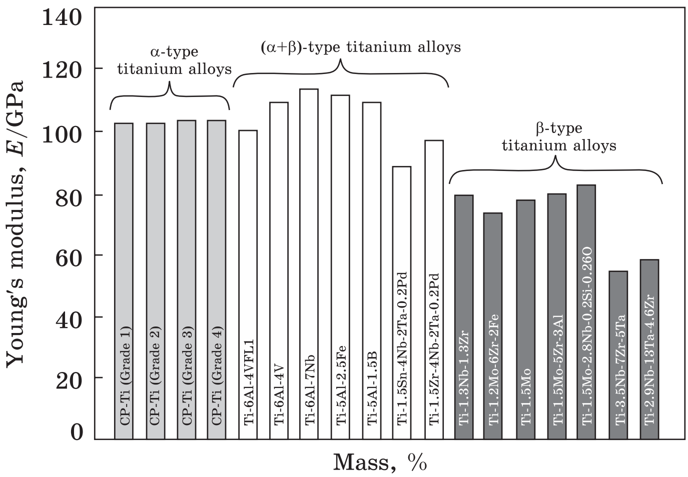

Fig. 4. Young's moduli for typical α, (α + β), and β biomedical alloys [38]

single-phase structures contributes to higher corrosion resistance in the human body, which allows solving certain problems in the use of biomedical materials [44, 45].

One of the methods for predicting the stability of the β-phase in the development of appropriate chemical compositions is the DV-X_α cluster technique (Fig. 5). This technique allows determining two parameters: the bonding order (B_o) and the energy level of the *d*-orbitals in metals (M_d). The bonding order is a measure of the strength of the bond between titanium and an alloying element, while M_d is related to the electronegativity and metal radii of the alloying elements [46]. In alloys, the average values of the bond order and energy level of the *d*-orbitals can be found as follows [47, 48]:

$$B_o = \sum_i X_i (B_o)_i, \quad M_d = \sum_i X_i (M_d)_i,$$

where X_i is the atomic percentage of element *i* in the alloy [47, 48]. Using this method, a phase stability map was plotted; see Fig. 5 [9]. The position of an alloy in the diagram varies depending on its chemical composition. In particular, this technique was used to develop several new β-alloys based on the systems Ti–Fe–Ta, Ti–Fe–Nb, Ti–Zr–Fe–Cr, Ti–Zr–Fe–Mn, and Ti–Nb–Fe–Cr [49–53].

A number of the developed β-Ti alloys, along with β-stabilizing alloying elements, contain zirconium in the amount of 4–13%, which both contributes to the strengthening of titanium by the solid-solution mechanism and is also one of the most biocompatible elements (Fig. 2). In general, many properties of titanium and zirconium are similar. Both of these elements have high inertness in biological tissues due to passivating the surface with the instantaneous formation of thin oxide scales (TiO_2, ZrO_2) [54]. When the surface oxide layer is destroyed, the rapid formation of a new passivation scale protects against further corrosion [55]. This gives the alloys based on the Ti–Zr system an advantage in the biomedical industry, as well as under conditions of exposure to aggressive environments.

Both of these metals have the α-h.c.p. lattice at room temperature. Therefore, the binary alloys of the Ti–Zr system have a single α-phase

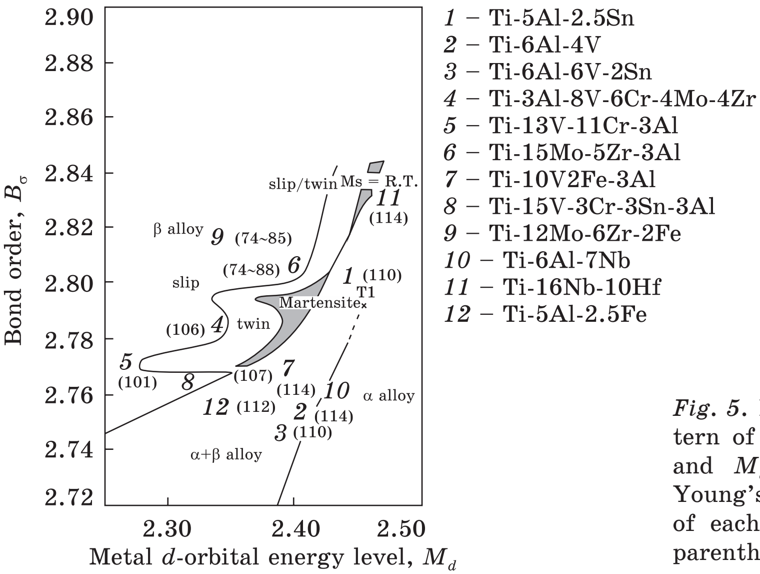

Fig. 5. Phase stability pattern of alloys based on B_o and M_d parameters. The Young's modulus (in GPa) of each alloy is shown in parentheses [9]

state, so they have rather high values of the Young's modulus (about 90–115 GPa), and their strength/ductility balance cannot be significantly changed with heat treatment [56]. Hence, Ti–Zr binary alloys have a very limited potential for implant manufacturing [57], so the development of more complex compositions is needed.

The above reasons promoted the development of biocompatible alloys based on the Ti–Zr system with a b.c.c. β-phase structure stabilized at room temperature by adding significant amounts of non-toxic β-stabilizers (such as Nb and Ta). These compositions provide a low elastic modulus and increased biocompatibility [58, 59]. It is alloys based on the above elements that are most widely developed and practically implemented. In particular, much attention is paid to the development of high-alloyed materials based on the Ti–Zr–Nb system with a low elastic modulus for medical needs (implant manufacturing), as well as for mechanical engineering for the manufacturing of elastic elements designed to work in chemically and corrosively aggressive environments [57].

3. High-Alloyed Medical Materials Based on Ti–Zr System

Titanium, zirconium, niobium, and tantalum have the best biocompatibility properties, which determine their choice as optimal materials for the manufacture of orthopaedic, dental and other implants. These elements are most often added to the high-alloyed medical materials with a b.c.c. β-structure [38, 60]. The zirconium–titanium binary system has a continuous series of solid solutions (Fig. 6) [61]. These metals are usually neutral strengtheners to each other; however, it is known [62, 63] that zirconium

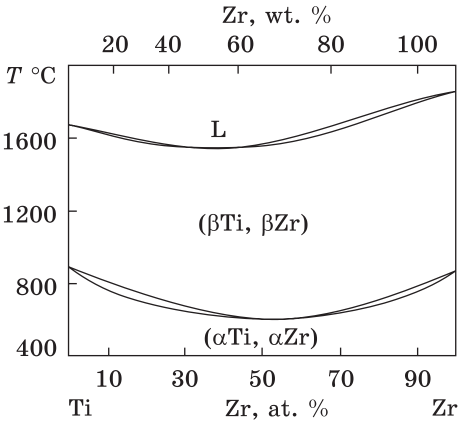

Fig. 6. Ti–Zr phase diagram [61]

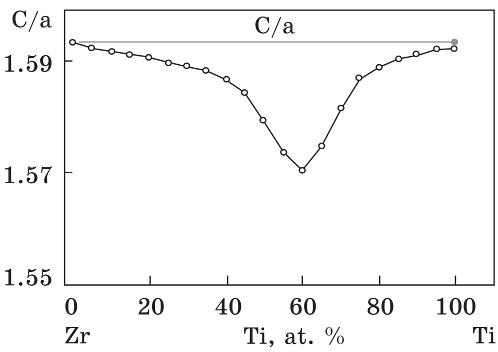

Fig. 7. The lattice parameters *c/a* ratio vs. the chemical composition of Ti–Zr binary alloys [71]

acts as a β-stabilizer in titanium in the presence of niobium. According to Ref. [64], the β-stabilizing effect of zirconium in the Ti–Nb system is observed in a wide concentration range of 6–50% Zr, increasing with the content of both zirconium and niobium. This makes it possible to increase the stability of the b.c.c.-β lattice of Ti–Zr–Nb alloys, avoiding the precipitation of the aI-martensite and w-phase at relatively low niobium content (10–14%), or when the concentrations of Zr and Nb change within a wide range. It should be emphasized that the possible precipitation of the aI-martensite or w-phase significantly increases the elastic modulus of the alloy, so, it is extremely undesirable for biomedical materials. Alloying titanium with a significant amount of zirconium and niobium simultaneously provides a number of advantages [64]. In particular, the Zr addition to the Ti–Nb β-alloys is effective in increasing the superelasticity, the maximum recovered strain, and the critical resolved shear stress [46, 65–67]. Niobium is used not only due to its β-stabilizing and strengthening effect on Ti–Zr alloys, but also due to its ability to stabilize the passivation oxide scale on the surface of biomedical alloys. This is provided by reducing the concentration of anion vacancies [68], which makes it possible to increase the corrosion resistance of the material in the human body. That is why Ti–Zr–Nb alloys have excellent corrosion resistance [69]. Changes in the contents of alloying elements in the ternary Ti–Zr–Nb system allow adjusting mechanical properties in wide ranges: for example, the strength of 316L stainless steel can be achieved [39], which is important for practical use.

As for biomedical compositions of the Ti–Zr system, the most promising are those close to equiatomic ones with the addition of niobium in the amount necessary to stabilize the β-phase [70]. The binary Ti–Zr compositions close to equiatomic [71, 72] have particular physical and mechanical properties, including the minimum melting point and the temperature of

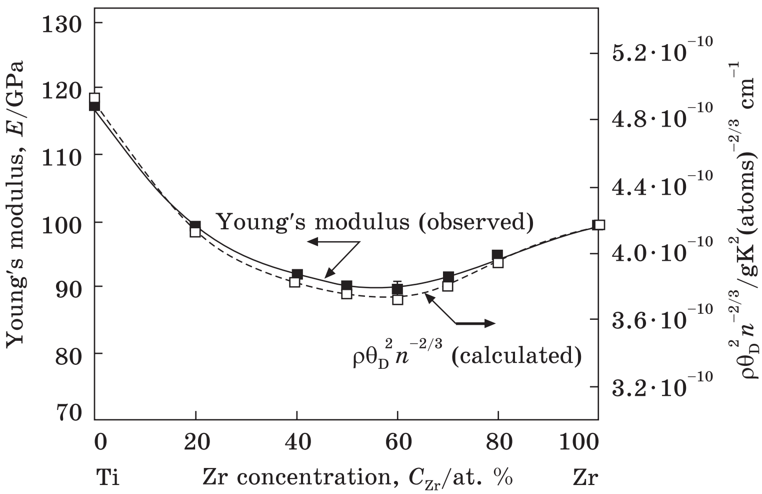

Fig. 8. Dependence of Young's modulus on zirconium content in the Ti–Zr binary system [72]

$\alpha\leftrightarrow\beta$-phase transformation (Fig. 6), as well as the minimum ratio of c/a parameters in the h.c.p. lattice (Fig. 7) [71].

According to the literature data [72], the lowest values of the elastic modulus of about 90 GPa were observed for binary Ti–Zr compositions close to equiatomic (Fig. 8). It was shown that the Young's modulus E is proportional to the Debye temperature θ_D [73]:

$$E \propto \rho\theta_D^2 n^{-2/3} .$$

The authors of [72] calculated the value of $\rho\theta_D^2 n^{-2/3}$ for various alloys and experimentally measured the Young's modulus. The lowest values of the Young's modulus for the Ti–Zr binary system lay in the range of ≈50–60 at.% Zr (Fig. 8). Therefore, this concentration range is considered the most promising for additional alloying to further reduce the elastic modulus in the development of low-modulus compositions.

The further reduction of the Young's modulus can be provided by the formation of a single β-phase state (b.c.c. structure) at room temperature, since this type of lattice has a lower elastic modulus compared to the h.c.p. α-phase [74]. Stabilization of the high-temperature b.c.c.-phase at room temperature in medical alloys is achieved by introducing a sufficient amount of β-stabilizers, usually niobium or tantalum, and less often molybdenum. In Ref. [75], using first-principles calculations and data of Refs. [76, 77], it was shown (Fig. 9) that varying the contents of components makes it possible to change the value of the Young's modulus within a fairly wide range (43–70 GPa) in the alloys of the Ti–Zr–Nb system. According to theoretical calculations, the 55.5Ti–26Zr–18.5Nb (at.%) composition was considered as the most promising for achieving a low Young's modulus (43 GPa).

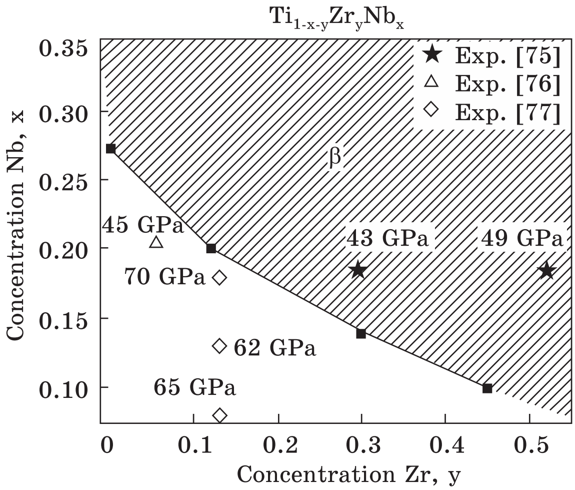

Fig. 9. The Zr- and Nb-content dependent Young's modulus in the Ti–Zr-based alloy [75–77]

Experimental studies in Refs. [71, 78] made it possible to develop a number of promising alloys based on the Ti–Zr–Nb system for medical applications. The choice of concentrations of alloying elements was based on the principle of optimal mismatches of the atomic radii of titanium, zirconium and niobium, which determine the average distance and bonding forces between atoms in the alloy lattice. The strength of the interatomic bond, in turn, determines the Young's modulus and other physical properties of the material, particularly the temperature of the α↔β-transformation. The determination of the mismatch was based on the fact that titanium and niobium have close atomic radii, whereas the zirconium atom has a significantly larger radius (Zr—≈0.160 nm, Ti—≈0.146 nm, and Nb—≈0.145 nm) [79]. This allowed determining the concentrations corresponding to the minimum temperature of the α↔β-transformation, and the conditions for obtaining a sufficiently stable β-phase with a low Young's modulus. According to Ref. [78], deviations from the recommended concentrations of titanium and niobium lead to a violation of the required dimensional heterogeneity, and, as a result, to a loss of the stability of the β-phase and an increase in the Young's modulus.

Recently, optimal medical compositions based on the Ti–Zr–Nb system have been considered in many works [80–85]; based on theoretical calculations and experimental studies, the authors proposed several compositions with Young's moduli at the level of 40–60 GPa, and in some cases, even lower values were reported.

It is worthwhile to note that some promising biomedical compositions based on the Ti–Zr–Nb system with b.c.c.-lattice contain another β-stabilizer, tantalum [86–90]. The addition of tantalum is useful [91, 92] both for strengthening alloys and for high biocompatibility. Like niobium, tantalum contributes to the formation of a passivation scale on the alloy surface, increasing corrosion resistance. According to [93], for alloys of the Ti–Zr–Nb-Ta system, the level of tantalum concentration should be maintained within a certain range; a slight deviation from this range increases the Young's modulus. The alloys of the Ti–Zr–Nb-Ta system with tantalum concentrations of 0–20 at.% were studied in Ref. [93]; the minimum

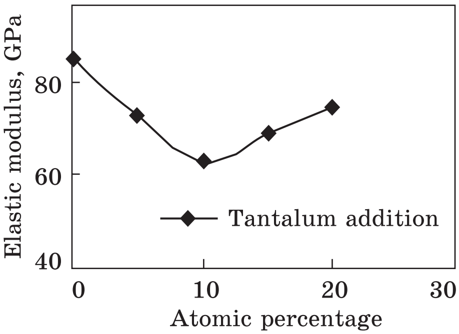

Fig. 10. The Ta-at.%-dependent Young's modulus in Ti–Zr–Nb–Ta [2]

value of the Young's modulus was observed at 10 at.% of Ta (Fig. 10). Such a nonlinear dependence of the Young's modulus is explained by the precipitation of the ω-phase at low tantalum concentrations. The ω-phase increases the elastic modulus, while the low modulus at 10 at.% Ta is associated with the single β-phase state. On the other hand, despite the single β-phase state is fixed at 15–20 wt.% Ta, the elastic modulus increases again due to the high Ta content. At high tantalum content, the alloy tends to behave like pure tantalum, so the material has a high Young's modulus close to that of this metal.

4. Features of the Phase and Structural States' Formation in Ti–Zr Alloys Produced from Powders

The specific characteristics of titanium and zirconium, such as the high ability of their surface to react with oxygen and other atmospheric impurities [94–97], especially when heated, determine the technological difficulties of manufacturing alloys (including biomedical ones) based on these metals. Typically, these alloys are produced by a complex technique of multiple vacuum remelting with subsequent multistage cold or hot deformation and heat treatment (Fig. 11) [98–101]. This provides homogeneity of chemical composition of the material, its microstructure and properties. However, the high cost of starting metals (titanium, zirconium, and alloying elements such as niobium and tantalum) and their high melting points significantly complicate the ingot production [102]; vacuum casting and hot deformation also increase the cost of materials. Besides, when producing alloys of different compositions using conventional casting techniques, the following problems can be encountered: evaporation of some alloying elements during melting; segregation of components during liquid phase solidification and ingot cooling; uncontrolled grain growth.

Alternative techniques of producing alloys that not only solve the abovementioned problems but also significantly reduce the cost of the materials are the methods of powder metallurgy [103, 104]. However, alloys made using powder technologies have comparatively high impurity content and pores, which often leads to a decrease in certain mechanical, physical, or performance characteristics of the final material. Therefore, studies [105–109] on the production of titanium and zirconium alloys

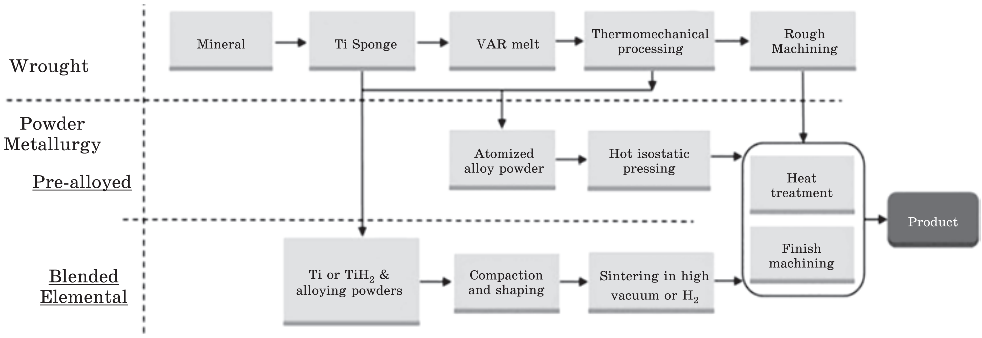

Fig. 11. Flow chart of conventional cast-wrought and powder metallurgy approaches for manufacturing Ti products [110]

from powder materials aimed to develop fundamentally new technological solutions that would not only significantly reduce the cost of production of these materials, but also form optimized structural and phase states while keeping the content of impurities at an acceptable level. This should provide the necessary complex of physical and mechanical properties of the materials.

Technologically, the simplest and, accordingly, cheapest method is to produce Ti- and Zr-based alloys by solid-phase sintering of multicomponent powder mixtures [110]. This approach eliminates the processes of remelting components, as sintering occurs at temperatures below the melting points of the components, and, in the simplest version, without additional pressure or deformation (Fig. 11). However, it is necessary to achieve the needed phase and structural states of the sintered alloy, which would provide its target properties.

The main technological operations in the manufacture of alloys from powders usually include the preparation of powders and their mixtures, compaction and sintering in vacuum [111, 112]. The production of Ti- and Ti–Zr-based alloys using this approach involves the use of base powders blended with an appropriate amount of powders of alloying elements (as pure metals or master alloys) and their transformation into chemically and microstructurally homogeneous bulk alloys with target phase composition during high-temperature annealing in vacuum. Thus, the processes of sintering and chemical homogenization of the particle system occur simultaneously with the corresponding evolution of the microstructure, which is controlled by diffusion processes in the solid phase. The exception is some alloying systems (*e.g.*, Ti–Al, Ti–Fe, Ti–Mn [113–115]), in which liquid phases temporarily form during sintering, when low-melting-point components melt or eutectic compositions form during chemical homogenization of a system of mixed powders. The production of alloys from multicomponent powder systems has the following advantages [116]:

· the possibility of forming homogeneous alloys at solid-phase temperatures below the melting points of all components, which prevents excessive grain growth and chemical segregations;

· the possibility of manufacturing a homogeneous material from metals that differ significantly in melting points and have limited mutual solubilities;

· the ability to control and regulate the parameters of the porous structure of the alloys, since the increased surface porosity of medical materials is necessary in some cases for better contact of the implant with biological tissues;

· low material losses in the production of alloys by this method (7–10 %), and the possibility of using cheap starting powders and waste from the metallurgical industry, which helps to reduce costs.

Besides the above advantages, there are certain disadvantages of producing Ti- and Zr-based alloys using powder technology. Firstly, a developed specific surface of the starting powders, with their significant affinity to atmospheric impurities, poses a risk of excessive contamination of the final products [116]. Secondly, the final materials often contain residual porosity that cannot be removed [113, 117]. These factors affect the phase and structural state of the final alloys, deteriorating their mechanical properties. The minimization of these negative effects requires: the use of impurity-free starting powders and their reliable protection from contamination during the mixing, compacting and high-temperature sintering; the latter operation is carried out in a high vacuum or, less often, in an inert atmosphere [118]. Except for the purposeful manufacture of products with significant controlled porosity, it is important to reduce the volume fraction of pores to a minimum, or even to form pore-free states. This is a criterion for providing high mechanical performance [113]. For this purpose, the following approaches can be applied: optimization of the size of starting powder particles [119, 120]; complex techniques of powder compaction (in particular, cold and hot isostatic pressing) [121]; special methods of particle sintering (*e.g.*, pressure sintering) [122, 123]; use of additional hot deformation to modify the structure of the final alloys [124]. Despite this, as a rule, alloys produced by powder approaches contain about 1.0% of residual pores that cannot be completely eliminated due to various impurities [125].

5. Physical Bases of Application of Hydrogenated Powders to Manufacture Ti–Zr-Based Biomedical Alloys

To achieve minimum residual porosity, low content of impurities, target structure, and, accordingly, enhanced physical and mechanical properties of Ti- and Zr-based alloys produced by sintering multicomponent powder mixtures, an approach was developed that uses the positive effect of hydrogen as a temporary alloying element [117–119, 126–132]. The approach is based on the use of starting hydrogenated metal powders to activate the processes of forming alloys from multicomponent powder mixtures by means of only cold compaction and subsequent vacuum sintering without pressure or deformation.

This approach was pioneered on the example of titanium alloys [113, 117, 119, 131, 132], and later extended to zirconium alloys. The use of TiH_2 titanium hydride particles as the basis of powder mixtures was shown to have significant advantages over conventional titanium powder. In particular, titanium alloys produced using the hydride approach have a lower residual porosity (*i.e.*, higher density) and a better balance of mechanical properties than similar alloys produced using conventional non-hydrogenated titanium powder.

The physical foundations of the hydrogen approach [117, 132–135] and the reasons for the advantages of hydrogenated powders in alloy production [113, 115] are as follows (on the example of titanium). When titanium is heated in a hydrogen atmosphere, gas molecules dissociate into atoms on the metal surface. Then, atomic hydrogen, which is an interstitial impurity, quickly diffuses into the crystal lattice, saturating it to a certain concentration. The unique ability of hydrogen as a temporary alloying element lies in the possibility of its reverse removal from the metal to practically zero content by operating temperature, partial pressure, and exposure time [136–138].

The saturation of a metal with hydrogen significantly changes its phase composition, physical (density, electrical conductivity, *etc.*), and mechanical (strength, ductility, hardness, Young's modulus) properties [133]. Metal hydrides are brittle and rather low-strength materials compared to non-hydrogenated metals [134, 135]. These mechanical properties facilitate the production of hydride powders with a given size distribution. Besides, hydride particles are crushed into fine fragments under the pressing force, forming a special system of fine pores between the compressed particles, which promotes porosity healing during subsequent sintering [139–141]. The processes that occur during hydrogen desorption are especially important. When the temperature in a vacuum rises above 300–400 °C (consider the example of titanium), hydrogen is released from the metal crystal lattice, $MeH_2 \rightarrow \beta$-b.c.c. $\rightarrow \alpha$-h.c.p. transformations occur, accompanied by significant volumetric effects with an overall decrease in the volume of materials with a decrease in the concentration of hydrogen dissolved in them. These phase transformations significantly increase the defect density in the crystal lattice [142]. The presence of hydrogen in the metal lattice increases the equilibrium concentration of vacancies [143]. Besides, atomic hydrogen dissolved in the metal lattice is much more active than in its normal molecular state. Therefore, atomic hydrogen reduces the surface TiO_2 oxide scale during sorption-desorption cycles [132, 144, 145], which is always present on the surface of powder and is a barrier to mutual diffusion in the powder system ($TiO_2 + 4H = Ti + 2H_2O$).

The possibility of the above reaction (before the transition of hydrogen to the molecular state during desorption from the surface) was predicted by thermodynamic calculations, and first experimentally proved by mass-spectrometric analysis of gases released during heating of titanium hydride. These phenomena lead to a significant activation of diffusion processes that accelerate the sintering and chemical homogenization of multicomponent powder systems. Hydrogen also additionally purifies the powder system, reducing the final content of impurities such as oxygen, chlorine, and carbon [146]. At the same time, hydrogen is completely removed from the material during vacuum sintering, which eliminates the problem of hydrogen embrittlement. The final contents of impurities in the sintered alloys are at safe levels: hydrogen—0.002–0.003, oxygen — 0.15–0.20, chlorine — 0.001–0.015 wt.%. Thus, alloys produced using the hydride approach have lower residual porosity (1–2%), acceptable impurity content, and, as a result, significantly enhanced mechanical properties.

Similar to titanium, zirconium interacts with hydrogen: both of these metals have similar binary phase diagrams with hydrogen. Therefore, the activation of solid-phase sintering of zirconium hydride powder ZrH_2 [118, 147, 148] occurs according to the same physical principles as for titanium hydride, *i.e.*, due to a higher concentration of equilibrium vacancies in the presence of hydrogen [142], and increased density of lattice defects caused by phase transformations [142].

As shown in Ref. [118], the synergistic use of mixtures of two hydrides (titanium and zirconium) in the synthesis of binary Ti–Zr–based alloys allows enhancing the positive effect of hydrogen on diffusion-controlled sintering processes. In particular, a positive aspect is the noticeable difference in the desorption temperatures of hydrogen from zirconium (approximately 330–800 °C) and titanium (approximately 300–600 °C), so the addition of zirconium hydride allows extending the effect of hydrogen on the activation of sintering to higher temperatures. These results became the basis for the production of binary alloys of the Ti–Zr system from powders, as well as multicomponent materials based on this system. On the example of the 60% Zr–40% Ti composition, it was shown that the use of mixtures of the two hydrides allowed reaching the density 98–98.5% of the theoretical one (*i.e.*, the residual porosity was reduced to 1.5–2%), whereas the density was ≈95–96.5% (4.5–5% porosity), when conventional powders were used.

Obvious extension of these studies was the use of the hydride powder approach to produce low-modulus alloys of the Ti–Zr–Nb system for medical applications [116, 130, 149, 150]. Besides, some studies [151] have been conducted to test the hydride powder approach for the synthesis of

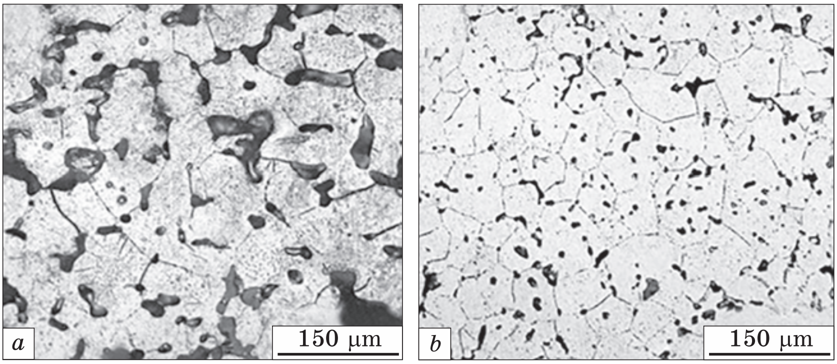

Fig. 12. Typical microstructures of Ti–Zr–Nb alloys produced from mixture ZrH_2 + TiH_2 + Nb (*a*) and ZrH_2 + TiH_2 + $(TiNb)H_x$ (*b*) [149]

nickel-containing alloys of the Zr–Ti–Ni system, which are promising materials for hydrogen batteries.

The main ways of producing alloys of the Ti–Zr–Nb system for biomedical applications were studied on the example of two compositions, 51Zr–31Ti–18Nb and 55.5Ti–26Zr–18.5Nb (wt.%), manufactured by pressing and vacuum sintering of powder mixtures [116, 130, 149]. Structurally homogeneous single b.c.c. β-phase alloys with low Young's modulus (55–56 GPa) were produced, which met the requirements for implant materials. At the same time, the residual porosity of sintered Ti–Zr–Nb alloys significantly depends on the type of starting powders. The alloys produced by sintering mixtures of two hydride powders and non-hydrogenated niobium powder (ZrH_2 + TiH_2 + Nb) had a significantly higher residual porosity (up to 6–11%; Fig. 12, *a*) than binary Ti–Zr alloys (1–3%) produced from the ZrH_2 + TiH_2 mixture. A significant volume fraction of pores is useful for reducing the Young's modulus; on the other hand, it leads to deterioration of strength and ductility, so the reasons for the increase in porosity and ways to control it were investigated.

Dilatometric measurements showed that an increase in the volume fraction of pores in compacted ZrH_2 + TiH_2 + Nb powder systems occurs during heating at the stage of hydrogen desorption from both hydrides due to drastically different size effects in the particles of hydrides and non-hydrogenated niobium. The sizes of hydride particles reduce when hydrogen is released, while niobium particles practically do not change their size. This mismatch of size effects between the hydrogenated and non-hydrogenated components of the mixtures causes the destruction of bonds between the particles and is the main reason for the increase in porosity during sintering of multicomponent alloys.

When the temperature further increases up to 1000–1250 °C, diffusion is activated and chemical homogenization occurs. The difference in diffusion fluxes between the system components leads to the development of porosity caused by the Kirkendall's effect, making an additional contribution to the increase in system porosity.

A possible way to reduce the volume fraction of pores (which is necessary for high strength and ductility) is to use exclusively hydrogenated powders in starting mixtures, which have similar size effects during hydrogen desorption, that should provide the integrity of the compacted powders.

Hydrogenated niobium is not stable, and loses hydrogen in a vacuum even at room temperature before heating [152]. Therefore, the use of this element in mixtures with zirconium and titanium hydrides did not have a noticeable effect on reducing the porosity in sintered Ti–Zr–Nb alloys. It is much more efficient to add niobium into the mixture in the form of particles of hydrogenated (Zr–Nb)H_x and (Ti–Nb)H_x master alloys [114, 149]. When heated at the stage of hydrogen desorption, the hydrogenated master alloys have a size effect similar to zirconium and titanium hydrides, which helps to preserve the integrity of the compacted powders and significantly enhances their shrinkage without increasing the volume of pores between the particles. Besides, the use of master alloys provides more uniform diffusion fluxes at the stage of chemical homogenization, which accelerates the achievement of microstructural homogeneity and reduces the negative impact of the Kirkendall's effect. The use of all hydrogenated powders made it possible to produce Ti–Zr–Nb alloys with a residual porosity of no more than 2% (Fig. 12, *b*).

Temporary alloying with hydrogen was also successfully used to produce a medical alloy containing tantalum—Ti–35Nb–7Zr–5Ta [149]. The clarification of the features of interaction of tantalum with hydrogen in Ref. [152] made it possible to use hydrogenated tantalum powder in starting mixtures. The hydrogenation of ductile tantalum embrittles it, promoting the production of fine powders of a given size fraction. The use of fine tantalum particles is necessary to accelerate the chemical homogenization of the powder system, given the extremely low diffusion mobility of this element ($5\cdot10^{-20}$ m^2/s at 1250 °C [150], *i.e.*, 7–8 orders of magnitude lower than the diffusion mobility of other elements Ti, Nb, and Zr [153] at the same temperature). Besides, hydrogen dissolved in tantalum gives an additional positive contribution to the processes of particle consolidation, when the compacted Ti–Zr–Nb–Ta powder mixture is heated in a vacuum. Despite the hydrogenation of the powders, the low diffusion mobility of tantalum did not allow for the achievement of its homogeneous distribution in the Ti–Zr–Nb matrix after sintering at 1250 °C. Therefore, the method of double compaction and sintering of hydrogenated powders was successfully used to provide a completely homogeneous structure of the Ti–35Nb–7Zr–5Ta alloy. After the first sintering of the hydrogenated powder mixture, the resulting inhomogeneous alloy was re-saturated with hydrogen, which made it brittle, and then ground into alloyed Ti–Nb–Zr–Ta powder particles, which were compacted and sintered again. This approach made it possible to produce a completely homogeneous alloy with porosity reduced to 2%.

All produced alloys had mechanical properties promising for practical application. For Ti–Zr–Nb materials produced with different blends, the hardness increased with reduction of residual porosity: 159 *HV* to 273 *HV* for 55.5Ti–26Zr–18.5Nb alloy, and 185 *HV* to 262 *HV* for 31Ti–51Zr–18Nb one. The Young's modulus values were determined for both these compositions with the highest porosity (6–9%); they were 55 GPa and 56.3 GPa, respectively. Such a relatively low Young's moduli are attractive for the production of medical implants. Tensile properties also varied significantly depending on residual porosity: the ultimate tensile strength (UTS) and elongation are 630–660 MPa and 6–7%, respectively, for as-sintered materials with 6–9% porosity; however, they increase to 1135 MPa and 14.3% for completely pore-free materials after additional hot deformation is applied. The as-sintered Ti–35Nb–7Zr–5Ta alloy had UTS of 1023–1053 MPa at elongation up to 16%. Therefore, the present approach provides sufficient mechanical properties and can be used to manufacture alloys and components for medical and other applications.

6. Conclusions

The paper summarizes the literature data on the requirements for modern metal materials for biomedical applications. It is noted that multicomponent Ti–Zr-based alloys with a single b.c.c. β-phase structure most fully meet the criteria of biocompatibility and the requirements for the mechanical properties of implant materials.

Promising achievements in the development of powder technologies for the production of low-modulus Ti–Zr–Nb and Ti–Zr–Nb–Ta β-alloys for medical applications are reviewed. The positive effect of hydrogen as a temporary alloying element in the hydrogenated powders of these metals is shown. Hydrogen promotes the homogenization of the structure of the alloys during sintering and the achievement of acceptable mechanical properties, including a sufficient strength level and an elastic modulus reduced to 55–56 GPa.

REFERENCES

1. N. Eliaz, Corrosion of Metallic Biomaterials: A Review, *Materials*, **12**, No. 3: 407 (2019); https://doi.org/10.3390/ma12030407
2. M. Geetha, A. Singh, R. Asokamani, and A. Gogia, Ti Based Biomaterials, the Ultimate Choice for Orthopaedic Implants — A Review, *Prog. Mater. Sci.*, **54**, No. 3: 397–425 (2009); https://doi.org/10.1016/j.pmatsci.2008.06.004
3. Z. Li, D. Liang, C. Zhong, T. Wan, W. Zhu, J. Luo, J. Yan, and F. Ren, Comprehensive Evaluation of Corrosion Resistance and Biocompatibility of Ultrafine-Grained TiMoNb Alloy for Dental Implants, *J Mater. Sci. Technol.*, **221**: 247–259 (2025); https://doi.org/10.1016/j.jmst.2024.09.030

4. S. Shimizu, T. Fujii, and Y. Shimamura, Development of Short-Titanium-Fiber-Reinforced Porous Titanium as Biometal for Implants. *J. Compos. Sci.*, **9**: 10 (2025); https://doi.org/10.3390/jcs9010010
5. M. Araya, A. Jдгvenрдд, T. Rautio, R. Vindas, R. Estrada, M. de Ruijter, and T. Guillén, *In-vivo* and *Ex-vivo* Evaluation of Bio-inspired Structures Fabricated via PBF-LB for Biomedical Applications, *Mater. Today Bio*, **31**: 101450 (2025); https://doi.org/10.1016/j.mtbio.2025.101450
6. W. Abd-Elaziem, M.A. Darwish, A. Hamada, and W.M. Daoush, Titanium-Based Alloys and Composites for Orthopedic Implants Applications: A Comprehensive Review, *Mater. Des.*, **241**: 112850 (2024); https://doi.org/10.1016/j.matdes.2024.112850
7. P. Baskaran, B. Muthiah, and V. Uthirapathy, A Systematic Review on Biomaterials and their Recent Progress in Biomedical Applications: Bone Tissue Engineering, *Rev. Inorganic Chem.*, **45**, No. 2: 411–436 (2025); https://doi.org/10.1515/revic-2024-0062
8. F. Günther, F. Hirsch, S. Pilz, M. Wagner, A. Gebert, M. Kästner, and M. Zimmermann, Structure-Property Relationships of Imperfect Additively Manufactured Lattices Based on Triply Periodic Minimal Surfaces, *Mater. Des.*, **222**: 111036 (2022); https://doi.org/10.1016/j.matdes.2022.111036
9. D. Kuroda, M. Niinomi, M. Morinaga, Y. Kato, and T. Yashiro, Design and Mechanical Properties of new β Type Titanium Alloys for Implant Materials, *Mater. Sci. Eng. A*, **243**, Nos. 1–2: 244–249 (1998); https://doi.org/10.1016/S0921-5093(97)00808-3
10. L. Liu, C. Yang, F. Wang, S. Qu, X. Li, W. Zhang, Y. Li, and L. Zhang, Ultrafine Grained Ti-based Composites with Ultrahigh Strength and Ductility Achieved by Equiaxing Microstructure. *Mater. Des.*, **79**: 1–5 (2015); https://doi.org/10.1016/j.matdes.2015.04.032
11. Y. Zhang, X. Wang, W. Zhang, W. Huo, J. Hu, and L. Zhang, Elevated Tensile Properties of Ti–O Alloy with a Novel Core-shell Structure, *Mater. Sci. Eng. A*, **696**: 360–365 (2017); https://doi.org/10.1016/j.msea.2017.04.088
12. L. Zhang and L. Chen, A Review on Biomedical Titanium Alloys: Recent Progress and Prospect, *Adv. Eng. Mater.*, **21**, No. 4: 1801215 (2019); https://doi.org/10.1002/adem.201801215
13. T. Odaira, S. Xu, K. Hirata, X. Xu, T. Omori, K. Ueki, K. Ueda, T. Narushima, M. Nagasako, S. Harjo, T. Kawasaki, L. Bodnбrovб, P. Sedlбk, H. Seiner, and R. Kainuma, Flexible and Tough Superelastic Co–Cr Alloys for Biomedical Applications, *Adv. Mater.*, **34**, No. 27: 2202305 (2022); https://doi.org/10.1002/adma.202202305
14. B. Ca, M. Xue, D. Yuan, X. Zhou, Y. Huang, and Z. Guo, Design of a Versatile Platform on Nanostructured Ti–Mo–Zr Alloy Surface with Photothermal, Antibacterial and Osteoinductive Properties for Biomedical Application, *Colloids Surf. B: Biointerfaces*, **248**: 114473 (2025); https://doi.org/10.1016/j.colsurfb.2024.114473
15. N. Hallab, S. Anderson, T. Stafford, T. Glant, and J. Jacobs, Lymphocyte Responses in Patients with Total Hip Arthroplasty, *J Orthop. Res.*, **23**, No. 2: 384–391 (2005); https://doi.org/10.1016/j.orthres.2004.09.001
16. A. Sargeant and T. Goswami, Hip implants: Paper V. Physiological effects, *Mater. Des.*, **27**, No. 4: 287–307 (2006); https://doi.org/10.1016/j.matdes.2004.10.028

17. R.K. Mishra and S.S. Singh, Comprehensive Review of Biological Response, Alloy Design, Strengthening Mechanisms, Performance Evaluation, and Surface Modifications of Titanium Alloys for Biomedical Applications, *Multiscale and Multidiscip. Model. Exp. and Des.*, **8**: 67 (2025); https://doi.org/10.1007/s41939-024-00658-2
18. E. Karamian, K.M. Motamedi, A. Khandan, P. Soltani, and S. Maghsoudi, An *in vitro* Evaluation of Novel NHA/zircon Plasma Coating on 316L Stainless Steel Dental Implant, *Prog. Natural Sci.: Mater. Int.*, **24**, No. 2: 150–156 (2014); https://doi.org/10.1016/j.pnsc.2014.04.001
19. https://www.upmet.com/sites/default/files/datasheets/316-316l.pdf
20. https://www.azom.com/article.aspx?ArticleID=2868
21. G.L. Winters and M.J. Nutt, Stainless Steels for Medical and Surgical Applications (ASTM International: 2003); https://doi.org/10.1520/STP1438-EB
22. A. Chiba, K. Kumagai, N. Nomura, and S. Miyakawa, Pin-on-disk Wear Behavior in a Like-on-like Configuration in a Biological Environment of High Carbon Cast and Low Carbon Forged Co–29Cr–6Mo Alloys, *Acta Mater.*, **55**: 1309 (2007); https://doi.org/10.1016/j.actamat.2006.10.005
23. M. Long and H. Rack, Titanium Alloys in Total Joint Replacement — a Materials Science Perspective, *Biomaterials*, **19**, No. 18: 1621–1639 (1998); https://doi.org/10.1016/S0142-9612(97)00146-4
24. Y.S. Al. Jabbari, Physico-Mechanical Properties and Prosthodontic Applications of Co–Cr Dental Alloys: a Review of the Literature, *J. Adv. Prosthodont.*, **6**, No. 2: 138–145 (2014); https://doi.org/10.4047/jap.2014.6.2.138
25. Y. Okazaki and E. Gotoh, Comparison of Metal Release from Various Metallic Biomaterials *in Vitro*, *Biomaterials*, **26**, No. 1: 11–21 (2005); https://doi.org/10.1016/j.biomaterials.2004.02.005
26. D.B. McGregor, R.A. Baan, C. Partensky, J.M. Rice, and J.D. Wilbourn, Evaluation of the Carcinogenic Risks to Humans Associated with Surgical Implants and other Foreign Bodies — a Report of an IARC Monographs Programme Meeting, *Eur. J. Cancer*, **36**, No. 3: 307–313 (2000); https://doi.org/10.1016/s0959-8049(99)00312-3
27. G Genchi, A. Carocci, G. Lauria, M. Stefania Sinicropi, and A. Catalano, Nickel: Human Health and Environmental Toxicology, *Int. J. Environ. Res. Public Health*, **17**, No. 3: 679 (2020); https://doi.org/10.3390/ijerph17030679
28. Q. Chen and G.A. Thouas, Metallic Implant Biomaterials, *Mater. Sci. Eng.: R: Reports*, **87**: 1–57 (2015); https://doi.org/10.1016/j.mser.2014.10.001
29. A. Prasad, N.L. Church, and N.G. Jones, An Investigation into the Ti–Nb–Ag Ternary System for Biocompatible Superelastic Alloys, *Metals*, **14**, No. 12: 1426 (2024); https://doi.org/10.3390/met14121426
30. https://www.carpentertechnology.com/hubfs/7407324/Material%20Saftey%20Data%20Sheets/Ti%20CP%20Grade%202.pdf
31. G. Lutjering and J.C. Williams, *Titanium* (Berlin–Heidelberg: Springer: 2007); https://doi.org/10.1007/978-3-540-73036-1
32. S. Tamilselvi, V. Raman, and N. Rajendran, Corrosion Behaviour of Ti–6Al–7Nb and Ti–6Al–4V ELI Alloys in the Simulated Body Fluid Solution by Electrochemical Impedance Spectroscopy, *Electrochim. Acta*, **52**: 839–846 (2006); https://doi.org/10.1016/j.electacta.2006.06.018

33. U. Zwicker and J. Breme, Investigations of the Friction Behaviour of Oxidized Ti–5% Al–2.5% Fe Surface Layers on Implant Material, *J. Less Com. Met.*, **100**: 371–375 (1984);
https://doi.org/10.1016/0022-5088(84)90076-6
34. M.A. Khan, R.L. Williams, and D.F. Williams, The Corrosion Behaviour of Ti–6Al–4V, Ti–6Al–7Nb and Ti–13Nb–13Zr in Protein Solutions, *Biomaterials*, **20**, No. 7: 631–637 (1999);
https://doi.org/10.1016/S0142-9612(98)00217-8
35. X. Lei, L. Dong, Z. Zhang, Y. Liu, Y. Hao, R. Yang, and L. Zhang, Microstructure, Texture Evolution and Mechanical Properties of VT3-1 Titanium Alloy Processed by Multi-Pass Drawing and Subsequent Isothermal Annealing, *Metals*, **7**, No. 4: 131 (2017);
https://doi.org/10.3390/met7040131
36. A. McAndrew, P. Colegrove, C. Bьhr, B. Flipo, and A. Vairis, A Literature Review of Ti–6Al–4V Linear Friction Welding, *Prog. Mater. Sci.*, **92**: 225–257 (2018);
https://doi.org/10.1016/j.pmatsci.2017.10.003
37. S. Huang, Q. Zhao, C. Wu, C. Lin, Y. Zhao, W. Jia, and C. Mao, Effects of β-Stabilizer Elements on Microstructure Formation and Mechanical Properties of Titanium Alloys, *J. Alloys Compd.*, **876**: 160085 (2021);
https://doi.org/10.1016/j.jallcom.2021.160085
38. M. Niinomi, Y. Liu, M. Nakai, H. Liu, and H. Li, Biomedical Titanium Alloys with Young's Moduli Close to that of Cortical Bone, *Regener. Biomater.*, **3**, No. 3: 173–185 (2016);
https://doi.org/10.1093/rb/rbw016
39. A. Biesiekierski, J. Lin, Y. Li, D. Ping, Y. Yamabe-Mitarai, and C. Wen, Investigations into Ti–(Nb,Ta)–Fe Alloys for Biomedical Applications, *Acta Biomater.*, **32**: 336–347 (2016);
https://doi.org/10.1016/j.actbio.2015.12.010
40. P. Fernandes Santos, M. Niinomi, H. Liu, K. Cho, M. Nakai, A. Trenggono, S. Champagne, H. Hermawan, and T. Narushima, Improvement of Microstructure, Mechanical and Corrosion Properties of Biomedical Ti–Mn Alloys by Mo Addition, *Mater. Des.*, **110**: 414–424 (2016);
https://doi.org/10.1016/j.matdes.2016.07.115
41. P. Ibrahim, R. Garrard, P. Penchev, K. Man, S.C. Cox, S. Dimov, and M.M. Attallah, Hybrid Manufacturing and Performance Evaluation of β Ti-Alloy Stents, *Mater. Des.*, **247**: 113420 (2024);
https://doi.org/10.1016/j.matdes.2024.113420
42. A. Ramarolahy, P. Castany, F. Prima, P. Laheurte, I. Péron, and T. Gloriant, Microstructure and Mechanical Behavior of Superelastic Ti–24Nb–0.5O and Ti–24Nb–0.5N Biomedical Alloys, *J. Mech. Behav. Biomed. Mater.*, **9**: 83–90 (2012);
https://doi.org/10.1016/j.jmbbm.2012.01.017
43. M. Besse, P. Castany, and T. Gloriant, Mechanisms of Deformation in Gum Metal TNTZ-O and TNTZ Titanium Alloys: A Comparative Study on the Oxygen Influence, *Acta Mater.*, **59**, No. 15: 5982–5988 (2011);
https://doi.org/10.1016/j.actamat.2011.06.006
44. J. Chen and W. Tsai, In Situ Corrosion Monitoring of Ti–6Al–4V Alloy in H_2SO_4/HCl Mixed Solution Using Electrochemical AFM, *Electrochim. Acta*, **56**, No. 4: 1746–1751 (2011);
https://doi.org/10.1016/j.electacta.2010.10.024
45. A. Carman, L. Zhang, O. Ivasishin, D. Savvakin, M. Matviychuk, and E. Pereloma, Role of Alloying Elements in Microstructure Evolution and Alloying Elements

Behaviour During Sintering of a near-β Titanium Alloy, *Mater. Sci. Eng. A*, **528**, No. 31: 686–1693 (2011);
https://doi.org/10.1016/J.MSEA.2010.11.004
46. M. Abdel-Hady, K. Hinoshita, and M. Morinaga, General Approach to Phase Stability and Elastic Properties of β-Type Ti-Alloys Using Electronic Parameters, *Scripta Mater.*, **55**, No. 5: 477–480 (2006);
https://doi.org/10.1016/j.scriptamat.2006.04.022
47. C. Li, D. Lee, X. Mi, W. Ye, S. Hui, and Y. Lee, Phase Transformation and age Hardening Behavior of new Ti–9.2Mo–2Fe Alloy, *J. Alloys Compd.*, **549**: 152–157 (2013);
https://doi.org/10.1016/j.jallcom.2012.08.065
48. M. Ahmed, D. Wexler, G. Casillas, O. Ivasishin, and E. Pereloma, The Influence of β Phase Stability on Deformation Mode and Compressive Mechanical Properties of Ti–10V–3Fe–3Al Alloy, *Acta Mater.*, **84**: 124–135 (2015);
https://doi.org/10.1016/j.actamat.2014.10.043
49. S. Ehtemam-Haghighi, Y. Liu, G. Cao, and L. Zhang, Phase Transition, Microstructural Evolution and Mechanical Properties of Ti-Nb-Fe Alloys Induced by Fe Addition, *Mater. Des.*, **97**: 279–286 (2016);
https://doi.org/10.1016/j.matdes.2016.02.094
50. S. Haghighi, H. Lu, G. Jian, G. Cao, D. Habibi, and L. Zhang, Effect of α″ Martensite on the Microstructure and Mechanical Properties of Beta-Type Ti–Fe–Ta Alloys, *Mater. Des.*, **76**: 47–54 (2015);
https://doi.org/10.1016/j.matdes.2015.03.028
51. C. Rabadia, Y. Liu, L. Wang, H. Sun, and L. Zhang, Laves Phase Precipitation in Ti–Zr–Fe–Cr Alloys with High Strength and Large Plasticity, *Mater. Des.*, **154**: 228–238 (2018);
https://doi.org/10.1016/j.matdes.2018.05.035
52. C. Rabadia, Y. Liu, G. Cao, Y. Li, C. Zhang, T. Sercombe, H. Sun, and L. Zhang, High-Strength β Stabilized Ti–Nb–Fe–Cr Alloys with Large Plasticity, *Mater. Sci. Eng. A*, **732**: 368–377 (2018);
https://doi.org/10.1016/j.msea.2018.07.031
53. C. Rabadia, Y. Liu, S. Jawed, L. Wang, Y. Li, X. Zhang, T. Sercombe, H. Sun, and L. Zhang, Improved Deformation Behavior in Ti-Zr-Fe-Mn Alloys Comprising the *C*14 Type Laves and β Phases, *Mater. Des.*, **160**: 1059–1070 (2018);
https://doi.org/10.1016/j.matdes.2018.10.049
54. R. Antunes and M. de Oliveira, Corrosion Fatigue of Biomedical Metallic Alloys: Mechanisms and Mitigation, *Acta Biomater.*, **8**, No. 3: 937–962 (2012);
https://doi.org/10.1016/j.actbio.2011.09.012
55. R. Yazdi, H. Ghasemi, C. Wang, and A. Neville, Bio-Corrosion Behaviour of Oxygen Diffusion Layer on Ti–6Al–4V During Tribocorrosion, *Corros. Sci.*, **128**: 23–32 (2017);
https://doi.org/10.1016/j.corsci.2017.08.031
56. A. Ataee, Y. Li, M. Brandt, and C. Wen, Ultrahigh-Strength Titanium Gyroid Scaffolds Manufactured by Selective Laser Melting (SLM) for Bone Implant Applications, *Acta Mater.*, **158**: 354–368 (2018);
https://doi.org/10.1016/j.actamat.2018.08.005
57. H. Chen, S. Hu, L. Wang, and L. Deng, Directional Design and Preparation of Ti-Nb Based Alloys with Predicted High Strength and Low Modulus for Biomedical Applications: Insights from First-Principles Calculations, *Intermetallics*, **177**: 108580 (2025);
https://doi.org/10.1016/j.intermet.2024.108580

58. J.P. Luo, J.F. Sun, Y.J. Huang, J.H. Zhang, Y.D. Zhang, D.P. Zhao, and M. Yan, Low-Modulus Biomedical Ti–30Nb–5Ta–3Zr Additively Manufactured by Selective Laser Melting and its Biocompatibility, *Mater. Sci. Eng. C*, **97**: 275–284 (2019); https://doi.org/10.1016/j.msec.2018.11.077
59. R.L. Batalha, W.C. Batalha, L. Deng, T. Gustmann, S. Pauly, C.S. Kiminami, and P. Gargarella, Processing a Biocompatible Ti–35Nb–7Zr–5Ta Alloy by Selective Laser Melting, *J. Mater. Research*, **35**: 1143–1153 (2020); https://doi.org/10.1557/jmr.2020.90
60. M. Lin, X. Xiao, C. Xu, W. Lu, Y. Zhang, and W. Liao, A Nanostructured TiZrNbTaMo High-Entropy Alloy Thin Film with Exceptional Corrosion Properties for Biomedical Application, *Appl. Surf. Sci.*, **684**: 161859 (2025); https://doi.org/10.1016/j.apsusc.2024.161859
61. J.L. Murray, The Ti–Zr (Titanium–Zirconium) System, *Bull. Alloy Phase Diagr.*, **2**, No. 2: 197–201 (1981); https://doi.org/10.1007/BF02881478
62. X. Tang, T. Ahmed, and H.J. Rack, Phase Transformations in Ti–Nb–Ta and Ti–Nb–Ta–Zr Alloys, *J. Mater. Sci.*, **35**: 1805–1811 (2000); https://doi.org/10.1023/A:1004792922155
63. M. Geetha, A. Singh, K. Muraleedharan, A. Gogia, and R. Asokamani, Effect of Thermomechanical Processing on Microstructure of a Ti–13Nb–13Zr Alloy, *J. Alloys Compd.*, **329**, Nos. 1–2: 264–271 (2001); https://doi.org/10.1016/S0925-8388(01)01604-8
64. M. Abdel-Hady, H. Fuwa, K. Hinoshita, H. Kimura, Y. Shinzato, and M. Morinaga, Phase Stability Change with Zr Content in β-Type Ti–Nb Alloys, *Scripta Mater.*, **57**: 1000–1003 (2007); https://doi.org/10.1016/j.scriptamat.2007.08.003
65. J.I. Kim, H.Y. Kim, T. Inamura, H. Hosoda, and S. Miyazaki, Shape Memory Characteristics of Ti–22Nb–(2–8)Zr(at.%) Biomedical Alloys, *Mater. Sci. Eng. A*, **403**: 334–339 (2005); https://doi.org/10.1016/j.msea.2005.05.050
66. H.Y. Kim, H. Satoru, J.I. Kim, H. Hosoda, and S. Miyazaki, Mechanical Properties and Shape Memory Behavior of Ti–Nb Alloys, *Mater. Trans.*, **45**, No. 7: 2443–2448 (2004); https://doi.org/10.2320/matertrans.45.2443
67. S. Miyazaki, H.Y. Kim, and H. Hosoda, Development and Characterization of Ni-Free Ti-Base Shape Memory and Superelastic Alloys, *Mater. Sci. Eng. A*, **438–440**: 18–24 (2006); https://doi.org/10.1016/j.msea.2006.02.054
68. R. Dąbrowski and K. Sołek, Formation of Microstructure and Mechanical Properties of Ti13Nb13Zr Medical Titanium Alloy, *Int. J.Eng. Sci. Technol.*, **47**: 101547 (2023); https://doi.org/10.1016/j.jestch.2023.101547
69. E. Frutos, M. Karlнk, J.A. Jimйnez, H. Langhansovб, J. Lieskovskб, and T. Polcar, Development of new β/α″-Ti–Nb–Zr Biocompatible Coating with Low Young's Modulus and High Toughness for Medical Applications, *Mater. Des.*, **142**: 44–55 (2018); https://doi.org/10.1016/j.matdes.2018.01.014
70. A. Maya, D. Grana, A. Hazarabedian, G. Kokubu, M. Luppo, and G. Vigna, Zr–Ti–Nb Porous Alloys for Biomedical Application, *Mater. Sci. Eng. C*, **32**, No. 2: 321–329 (2012); https://doi.org/10.1016/j.msec.2011.10.035

71. O. Ivasishin, O. Karasevskaya, P. Markovsky, and I. Skiba, Possibilities of Creating a new Biocompatible Low-Modulus Alloy Based on Zr and Ti, *Abst. Int. Conf. Ti-2011 in CIS* (*April 25–28, 2011, Lviv*), p. 166–172 (in Russian).
72. T. Shiraishi, K. Yubuta, T. Shishido, and N. Shinozaki, Elastic Properties of As-Solidified Ti–Zr Binary Alloys for Biomedical Applications, *Mater. Trans.*, **57**, No. 12: 1986–1992 (2016);
https://doi.org/10.2320/matertrans.MI201501
73. M.A. Omar, *Elementary Solid State Physics. Principles and Applications* (Pearson Education: 2016).
74. W. Weng, A. Biesiekierski, J. Lin, S. Ozan, Y. Li, and C. Wen, Development of Beta-Type Ti–Nb–Zr–Mo Alloys for Orthopedic Applications, *Appl. Mater. Today*, **22**: 100968 (2021);
https://doi.org/10.1016/j.apmt.2021.100968
75. A. Timoshevskii, S. Yablonovskyy, and O. Ivasishin, First-Principles Calculations Atomic Structure and Elastic Properties of Ti–Nb Alloys, *Funct. Mater.*, **19**, No. 2: 266–271 (2012);
https://doi.org/10.1016/10.15407/fm24.01
76. V. Brailovski, S. Prokoshkin, M. Gauthier, K. Inaekyan, S. Dubinskiy, M. Petrzhik, and M. Filonov, Bulk and Porous Metastable Beta Ti–Nb–Zr(Ta) Alloys for Biomedical Applications, *Mater. Sci. Eng. C*, **31**, No. 3: 643–657 (2011);
https://doi.org/10.1016/j.msec.2010.12.008
77. S. Schneider, S.G. Schneider, H. Marques da Silvab, C. de Moura Neto, Study of the Non-Linear Stress–Strain Behavior in Ti–Nb–Zr Alloys, *Mater. Res.*, **8**, No. 4: 435–438 (2005);
https://doi.org/10.1590/S1516-14392005000400013
78. O. Karasevska, I. Skiba, O. Ivasishin, and P. Markovsky, *Biosymisny Splav iz Nyzkym Modulem Pruzhnosti na Osnovi Systemy Zyrkonii–Tytan* [Biocompatible Alloy with Low Modulus of Elasticity Based on Zirconium Titanium System], Patent 102455 UA. MKI, A61L27/00, A61F2/02 (Published 10.07.2013) (in Ukrainian).
79. N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Elsevier Science & Technology Books: 2012).
80. H. Schaal, P. Castany, P. Laheurte, and T. Gloriant, Design of a Low Young's Modulus Ti–Zr–Nb–Sn Biocompatible Alloy by *in situ* Laser Powder bed Fusion Additive Manufacturing Process, *J. Alloys Compd.*, **966**: 171539 (2023);
https://doi.org/10.1016/j.jallcom.2023.171539
81. S.X. Liang, X.J. Feng, L.X. Yin, X.Y. Liu, M.Z. Ma, and R.P. Liu, Development of a New β Ti Alloy with Low Modulus and Favorable Plasticity for Implant Material, *Mater. Sci. Eng. C*, **61**: 338–343 (2016);
https://doi.org/10.1016/j.msec.2015.12.076
82. K.C. Nune, R.D. Misra, S.J. Li, Y.L. Hao, and R. Yang, Osteoblast Cellular Activity on Low Elastic Modulus Ti–24Nb–4Zr–8Sn Alloy, *Dent. Mater.*, **33**: 152–165 (2017);
https://doi.org/10.1016/j.dental.2016.11.005
83. L. Shi, L. Shi, L. Wang, Y. Duan, W. Lei, Z. Wang, J. Li, X. Fan, X. Li, S. Li, and Z. Guo, The Improved Biological Performance of a Novel Low Elastic Modulus Implant, *PLoS ONE*, **8**: e55015 (2013);
https://doi.org/10.1371/journal.pone.0055015
84. T. Zhang, P. Ou, J. Ruan, and H. Yang, Nb–Ti–Zr Alloys for Orthopedic Implants, *J. Biomater. Appl.*, **35**, No. 10: 1284–1293 (2021);
https://doi.org/10.1177/0885328220970756

85. O. Mishchenko, O. Ovchynnykov, O. Kapustian, and M. Pogorielov, New Zr-Ti-Nb Alloy for Medical Application: Development, Chemical and Mechanical Properties, and Biocompatibility, *Materials*, **13**, No. 6: 1306 (2020); https://doi.org/10.3390/ma13061306
86. N. Sumitomo, K. Noritake, T. Hattori, K. Morikawa, S. Niwa, K. Sato, and M. Niinomi, Experiment Study on Fracture Fixation with Low Rigidity Titanium Alloy, *J Mater Sci: Mater Med,* **19**, No. 4: 1581–1586 (2008); https://doi.org/10.1007/s10856-008-3372-y
87. I. Зaha, A.C. Alves, L.A. Rocha, and F. Toptan, A Review on Bio-Functionalization of β-Ti Alloys, *J. Bio Tribo. Corros.*, **6**: 135 (2020); https://doi.org/10.1007/s40735-020-00432-0
88. S. Ozan, J. Lin, Y. Li, and C. Wen, New Ti-Ta-Zr-Nb Alloys with Ultrahigh Strength for Potential Orthopedic Implant Applications, *J. Mech. Behav. Biomed. Mater.*, **75**: 119–127 (2017); https://doi.org/10.1016/j.jmbbm.2017.07.011
89. J. Strбský, P. Harcuba, K. Václavová, K. Horváth, M. Landa, O. Srba, and M. Janeček, Increasing Strength of a Biomedical Ti–Nb–Ta–Zr Alloy by Alloying with Fe, Si and O, *J. Mech. Behav. Biomed. Mater.*, **71**: 329–336 (2017); https://doi.org/10.1016/j.jmbbm.2017.03.026
90. W. Kong, S.C. Cox, Y. Lu, V. Villapun, X. Xiao, W. Ma, M. Liu, and M.M. Attallah, Microstructural Evolution, Mechanical Properties, and Preosteoblast Cell Response of a Post-Processing-Treated TNT5Zr β Ti Alloy Manufactured via Selective Laser Melting, *ACS Biomater. Sci. Eng.*, **8**: 2336–2348 (2022); https://doi.org/10.1021/acsbiomaterials.1c01277
91. T.Y. Wei, J.C. Huang, C.-Y. Chao, L.L. Wei, M.T. Tsai, and Y.H. Chen, Microstructure and Elastic Modulus Evolution of TiTaNb Alloys, *J. Mech. Behav. Biomed. Mater.*, **86**: 224–231 (2018); https://doi.org/10.1016/j.jmbbm.2018.06.047
92. R. Soni, S. Pande, S. Salunkhe, H. Natu, E. Abouel Nasr, R. Shanmugam, and H.M.A.M. Hussein, In Vitro and Electrochemical Characterization of Laser-Cladded Ti-Nb-Ta Alloy for Biomedical Applications, *Crystals*, **12**: 954 (2022); https://doi.org/10.3390/cryst12070954
93. N. Sakaguchi, M. Niinomi, T. Akahori, J. Takeda, and H. Toda, Relationships between Tensile Deformation Behavior and Microstructure in Ti–Nb–Ta–Zr System Alloys, *Mater. Sci. Eng. C*, **25**, No. 3: 363–369 (2005); https://doi.org/10.1016/j.msec.2004.12.014
94. O.G. Glotov, Combustion of Spherical Agglomerates of Titanium in Air. I. Experimental Approach, *Combust Explos Shock Waves*, **49**: 299–306 (2013); https://doi.org/10.1134/S0010508213030064
95. S. Sahoo, S. Pamir Alpay, and R.J. Hebert, Surface Phase Diagrams of Titanium in Oxygen, Nitrogen and Hydrogen Environments: A First Principles Analysis, *Surf. Sci.*, **677**: 18–25 (2018); https://doi.org/10.1016/j.susc.2018.05.007
96. W. Guldner and L. Wooten, Reactions of Zirconium with Gases at Low Pressure. *J. Electrochem. Soc.*, **93**, No. 6: 223 (1948); https://doi.org/10.1149/1.2773810
97. R.H. Nielsen, J.H. Schlewitz, and H. Nielsen, *Zirconium and Zirconium Compounds* (Kirk-Othmer Encyclopedia of Chemical Technology: 2013); https://doi.org/10.1002/0471238961.26091803.a01.pub3
98. X. Song, W. Ye, S. Hui, Y. Yu, R. Liu, Y. Fu, and X Mi, Low-Elastic-Modulus High-Strength Titanium Alloy and Preparation Method Thereof, MKI, C22C 14/00, C22C 1/02, C22C 1/18, Patent CN103173653B (Published 11.03.2015) (in Chinese).

99. S. Zhang, H. Wang, L. Ren, K. Yang, and Z. Sun, Medical Titanium Alloy Material for Reinforcing Anchorage Micro-Implant and Preparation Method Thereof, MKI, A61L 27/50, A61L 27/04, C22F 1/18, C22C 14/00, Patent CN110170069B (Published 09.11.2021) (in Chinese).
100. S. Zhang, H. Wang, L. Ren, and L. Ke, A Kind of Dedicated Medical Titanium Alloy of Planting Body and Preparation Method Thereof for Realizing Immediate Implant, MKI, C22F 1/18, A61L 27/50, A61L 27/06, Patent CN110157948B (Published 30.04.2021) (in Chinese).
101. J. Wang, N. Wu, S. Li, Y. Luo, Z. Yong, and J Yu, Method for Designing Low-Elasticity-Modulus Titanium Alloy, MKI, G06F 30/20, Patent CN107665274B (Published 05.18.2021) (in Chinese).
102. K. Narita, M. Niinomi, M. Nakai, J. Hieda, and K. Oribe, Development of Thermo-Mechanical Processing for Fabricating Highly Durable - Type Ti–Nb–Ta–Zr rod for use in Spinal Fixation Devices, *J. Mechan. Behav. Biomed. Mater.*, **9**: 207–216 (2012);
https://doi.org/10.1016/j.jmbbm.2012.01.011
103. F.H. Froes, S.J. Mashl, J.C. Hebeisen, V.S. Moxson, and V.A. Duz, The Technologies of Titanium Powder Metallurgy, *JOM*, **56**: 46–48 (2004);
https://doi.org/10.1007/s11837-004-0252-x
104. M. Qian, G. Schaffer, and C. Bettles, Sintering of Titanium and Its Alloys, *Sintering of Advanced Materials*, Iss. 3: 324–355 (2010);
https://doi.org/10.1533/9781845699949.3.324
105. M. Niinomi, Properties and Applications of Ti: Current Status and Future Needs, *Abstr. Int. Conf. Ti-2003, Proceedings of 10th World Conference on Titanium (July, 13–18, 2003, Hamburg)*, p. 95–110.
106. D. Eylon, W. Ernst, D. Kramer, and L. Jacobsen, Development of Ultra Fine Microstructure by Rapid Hot Compaction of Armstron-Process Titanium Powder, *Abstr. Int. Conf.* Ti-2007 *Science and technology*, *Proceedings of 11th World Conference on Titanium (June 3–7, 2007, Kyoto)*, p. 1145–1149.
107. J. de Monicault, J. Guedou, P. Belaygue, and V. Andre, Issues and Progress in Manufacturing of Turbo-Engines Titanium Parts, *Abstr. Int. Conf.* Ti-2007 *Science and technology*, *Proceedings of 11th World Conference on Titanium (June 3–7, 2007, Kyoto)*, p. 1301–1308.
108. M. Imam and F. Froes, Titanium Powder Metallurgy: Cost-Effective Developments, *Abstr. Int. Conf. Ti-2011 Science and Technology, Proceedings of the 12th World Conference on Titanium* (*Beijing: 2011*), p. 2223–2226.
109. L. Bolzoni, E. Herraiz, E.M. Ruiz-Navas, and E. Gordo, Development of Low-Cost Powder Metallurgy Titanium Alloys by Addition of Commercial 430 Stainless Steel Powder, *TMS 2014: 143rd Annual Meeting and Exhibition*, p. 597–604 (2014);
https://doi.org/10.1007/978-3-319-48237-8_72
110. Z.Z. Fang, J.D. Paramore, P. Sun, K.S. Ravi Chandran, Y. Zhang, Y. Xia, F. Cao, M. Koopman, and M. Free, Powder Metallurgy of Titanium — Past, Present, and Future, *Int. Mater. Rev.*, **63**, No. 7: 407–459 (2018);
https://doi.org/10.1080/09506608.2017.1366003
111. F.H. Froes and D. Eylon, Powder Metallurgy of Titanium Alloys, *Int. Mater. Rev.*, **35**, No. 1: 162–184 (1990);
https://doi.org/10.1179/095066090790323984
112. F.H. Froes, Titanium Powder Metallurgy: A Review, Pt. 1, *AM&P Technical Articles*, **170**, No. 9: 16–22 (2012);
https://doi.org/10.31399/asm.amp.2012-09.p016

113. O. Ivasishin, D. Savvakin, F. Froes, and K. Bondareva, Synthesis of Alloy Ti–6Al–4V with Low Residual Porosity by a Powder Metallurgy Method, *Powder Metall Met. Ceram.*, **41**, No. 7/8: 382–390 (2002); https://doi.org/10.1023/A:1021117126537
114. L. Bolzoni, T. Weissgaerber, B. Kieback, E. Ruiz-Navas, and E. Gordo, Mechanical Behaviour of Pressed and Sintered CP Ti and Ti–6Al–7Nb Alloy Obtained from Master Alloy Addition Powder, *J. Mechan. Behav. Biomed. Mater.*, **20**: 149–161 (2013); https://doi.org/10.1016/j.jmbbm.2012.08.022
115. D. Savvakin, A. Carman, O. Ivasishin, M. Matviychuk, A. Gazder, and E. Pereloma, Effect of Iron Content on Sintering Behavior of Ti–V–Fe–Al Near β Titanium Alloy, *Metall Mater. Trans. A*, **43**: 716–723 (2012); https://doi.org/10.1007/s11661-011-0875-9
116. D.V. Oryshych, *Phase and Structural Transformations on Hydrogen-Activated Synthesis of Zirconium-Based Alloys* (Diss. Ph.D. Degree of Physical and Mathematical Sciences) (Kyiv: G.V. Kurdyumov Institute for Metal Physics of the N.A.S. of Ukraine: 2021) (in Ukrainian).
117. O.M. Ivasishin and V.S. Moxson, Low Cost Titanium Hydride Powder Metallurgy, *Titanium Powder Metallurgy: Science, Technology and Applications* (Eds. M. Qian and F. Froes) (Elsevier: 2015).
118. D.G. Savvakin and M.M. Gumenyak, Synthesis of Alloys Based on Binary Zr–Ti System Using Dispersed Zirconium Hydride, *Metallofiz. Noveishie Tekhnol.*, **35**, No. 3: 1237–1252 (2013) (in Ukrainian).
119. O.M. Ivasishin, V.M. Anokhin, A.N. Demidik, and D.G. Savvakin, Cost-Effective Blended Elemental Powder Metallurgy of Titanium Alloys for Transportation Application, *Key Eng. Mater.*, **188**: 55–62 (2000); https://doi.org/10.4028/www.scientific.net/KEM.188.55
120. Y. Yang, S. Luo, G. Schaffer, and M. Qian, Sintering of Ti–10V–2Fe3Al and Mechanical Properties, *Mater. Sci. Eng. A*, **528**, Nos. 22–23: 6719–6726 (2011); https://doi.org/10.1016/j.msea.2011.05.041
121. M. Qian, Cold Compaction and Sintering of Titanium and its Alloys for Near-Net-Shape or Preform Fabrication, *Int. J. Powder Metall.*, **46**, No, 5: 29–44 (2010); https://doi.org/10.18307/2010.0104
122. F.H. Froes, O.N. Senkov, and J.I. Qazi, Hydrogen as a Temporary Alloying Element in Titanium Alloys: Thermohydrogen Processing, *Int. Mater. Rev.*, **49**, Nos. 3–4: 227–245 (2004); https://doi.org/10.1179/095066004225010055
123. C. Yu, P. Cao, and M.I. Jones, Titanium Powder Sintering in a Graphite Furnace and Mechanical Properties of Sintered Parts, *Metals*, **7**, No. 2: 67 (2017); https://doi.org/10.3390/met7020067
124. S. El-Soudani, K. Yu, E. Crist, F. Sun, M. Campbell, T. Esposito, J. Phillips, V. Moxson, and V. Duz, Optimization of Blended-Elemental Powder-Based Titanium Alloy Extrusions for Aerospace Applications, *Metall. Mater. Trans. A*, **44**, No. 2: 899–910 (2013); https://doi.org/10.1007/s11661-012-1437-5
125. A.A. Elhadad, L. Romero-Resendiz, M.C. Rossi, L.M. Rodrнguez-Albelo, S. Lascano, C.R.M. Afonso, A. Alcudia, V. Amigy, and Y. Torres, Findings and Perspectives of β-Ti Alloys with Biomedical Applications: Exploring Beyond Biomechanical and Biofunctional Behaviour, *J. Mater. Res. Technol.*, **33**: 3550–3618 (2024); https://doi.org/10.1016/j.jmrt.2024.09.248
126. O.M. Ivasishin, D.G. Savvakin, K.A. Bondareva, V.S. Moxson, and V.A. Duz, Production of Titanium Alloys and Components by Cost-Effective Powder

Metallurgy Approach for Wide Industrial Application, *Nauka Innov.*, **1**, No. 5: 44–57 (2005);
https://doi.org/10.15407/scin1.02.044
127. O. Ivasishin, D. Eylon, V. Bondarchuk, and D. Savvakin, Diffusion during Powder Metallurgy Synthesis of Titanium Alloys, *Defect Diffus. Forum*, **277**: 177–185 (2008);
https://doi.org/10.4028/www.scientific.net/DDF.277.177
128. G. Ma, T. Cheng, H. Jia, L. Yuan, O.M. Ivasishin, and D.G. Savvakin, A Novel Method to Fabricate high Strength and Ductility Ti–3Al–5Mo–4.5 V Alloy Based on TiH_2 and Pre-Hydrogenated Master Alloy Powders, *Mater. Des.*, **227**: 111791 (2023);
https://doi.org/10.1016/j.matdes.2023.111791
129. O.M. Ivasishin, O.P. Karasevska, D.G. Savvakin, M.M. Humenyak, Ya.I. Melnyk, and O.O. Stasiuk, Features of Volume Effects under a Heating of Compacted Powder of Zirconium Hydride, *Metallofiz. Noveishie Tekhnol.*, **38**, No. 11: 1527–1540 (2016) (in Ukrainian);
https://doi.org/10.15407/mfint.38.11.1527
130. D.V. Oryshych, O.M. Ivasishin, P.E. Markovsky, D.G. Savvakin, O.O. Stasiuk, and V.I. Bondarchuk, Peculiarities of Pore Structure Formation upon Zr–Ti–Nb Alloys Synthesis Using Hydrogenated Powder Blends, *Metallofiz. Noveishie Tekhnol.*, **42**, No. 12: 1681–1700 (2020) (in Ukrainian);
https://doi.org/10.15407/mfint.42.12.1681
131. O.M. Ivasishin and D.G. Savvakin, The Impact of Diffusion on Synthesis of High-Strength Titanium Alloys from Elemental Powder Blends, *Key Eng. Mater.*, **436**: 113–121 (2010);
https://doi.org/10.4028/www.scientific.net/KEM.436.113
132. D.G. Savvakin, *Physical Background of Solid State Synthesis of Titanium Alloys* (Diss. Doctor of Physical and Mathematical Sciences) (Kyiv: G.V. Kurdyumov Institute for Metal Physics of the N.A.S. of Ukraine: 2013) (in Ukrainian).
133. B. Kolachev, A. Ilyin, B. Lavrenko, and Yu. Levinsky, *Hydride Systems: Reference Book* (Moskva: Metallurgiya: 1991) (in Russian).
134. M.V. Goltsova, Hydrogen Technologies in Foundry and Metallurgy: Current State and Perspectives (Review), *Foundry Produc. Metal.*, No. 4: 145–154 (2018) (in Russian);
https://doi.org/10.21122/1683-6065-2018-4-145-154
135. Z. Fang, P. Sun, and H. Wang, Hydrogen Sintering of Titanium to Produce High Density Fine Grain Titanium Alloys, *Adv. Eng. Mater.*, **14**, No. 6: 383–387 (2012);
https://doi.org/10.1002/adem.201100269
136. V.A. Dekhtyarenko, D.G. Savvakin, V.I. Bondarchuk, V.M. Shyvaniuk, T.V. Pryadko, and O.O. Stasiuk, $TiMn_2$-Based Intermetallic Alloys for Hydrogen Accumulation: Problems and Prospects, *Prog. Phys. Met.*, **22**, No. 3: 307–351 (2021);
https://doi.org/10.15407/ufm.22.03.307
137. V.A. Dekhtyarenko, T.V. Pryadko, O.I. Boshko, V.V. Kirilchuk, H.Yu. Mykhailova, and V.I. Bondarchuk, Hydrogen Embrittlement of Titanium: Phenomena and Main Ways of Prevention, *Prog. Phys. Met.*, **25**, No. 2: 276–293 (2024);
https://doi.org/10.15407/ufm.25.02.276
138. V.G. Ivanchenko, V.A. Dekhtyarenko, T.V. Pryadko, D.G. Savvakin, and I.K. Evlash, Influence of Heat Treatment on the Hydrogen-Sorption Properties of $Ti_{0.475}Zr_{0.3}Mn_{0.225}$ Eutectic Alloy Doped with Vanadium, *Mater. Sci.*, **51**: 492–499 (2016);
https://doi.org/10.1007/s11003-016-9867-7

139. D.H. Savvakin, M.M. Humenyak, M.V. Matviichuk, and O.H. Molyar, Role of Hydrogen in the Process of Sintering of Titanium Powders, *Mater. Sci.*, **47**: 651–661 (2012);
https://doi.org/10.1007/s11003-012-9440-y
140. S. Dong, B. Wang, Y. Song, G. Ma, H. Xu, D. Savvakin, and O. Ivasishin, Comparative study on Cold Compaction Behaviour of TiH_2 Powder and HDH-Ti Powder, *Adv. Mater. Sci. Eng.*, **2021**: 9999541 (2021);
https://doi.org/10.1155/2021/9999541
141. S. Dong, G. Ma, P. Lei, T. Cheng, D. Savvakin, and O. Ivasishin, Comparative study on densification process of different titanium powder, *Adv. Powder Technol.*, **32**, No. 7: 2300–2310 (2021); https://doi.org/10.1016/j.apt.2021.05.009
142. O.M. Ivasyshyn, D.H. Savvakin, V.A. Dekhtyarenko, and O.O. Stasyuk, Interaction of Ti–Al–V–Fe, Al–V–Fe, and Ti–Al–Mo–Fe Powder Master Alloys with Hydrogen. *Mater. Sci.*, **54**: 266–272 (2018);
https://doi.org/10.1007/s11003-018-0182-3
143. Y. Fukai, Formation of Superabundant Vacancies in *M*–H Alloys and Some of Its Consequences: a Review, *J. Alloys Compd.*, **356–357**: 263–269 (2003);
https://doi.org/10.1016/S0925-8388(02)01269-0
144. V.G. Ivanchenko, V.A. Dekhtyarenko, and T.V. Pryadko, Hydrogen-sorption properties of (Ti, Zr)Mn_{2-x} intermetallic alloy, *Powder Metall. Met. Ceram.*, **52**: 340–344 (2013);
https://doi.org/10.1007/s11106-013-9531-9
145. V.A. Dekhtyarenko, T.V. Pryadko, T.P. Vladimirova, S.V. Maksymova, H. Yu. Mykhailova, and V.I. Bondarchuk, Effect of Alloying on the Hydrogen Sorption in Ti–Zr–Mn-Based Alloys. Pt. 1: *C*14-Type Laves-Phase-Based Alloys, *Prog. Phys. Met.*, **25**, No. 3: 520–544 (2024);
https://doi.org/10.15407/ufm.25.03.520
146. O.M. Ivasishin, D.G. Savvakin, M.M. Gumenyak, and A.B. Bondarchuk, Role of Surface Contamination in Titanium PM, *Key Eng. Mater.*, **520**: 121–132 (2012);
https://doi.org/10.4028/www.scientific.net/KEM.520.121
147. E. Pereloma, D. Savvakin, A. Carman, A. Gazder, and O. Ivasishin, Microstructure Development and Alloying Elements Diffusion during Sintering of Near-β Titanium Alloys, *Key Eng. Mater.*, **520**: 49–56 (2012);
https://doi.org/10.4028/www.scientific.net/KEM.520.49
148. D. Setoyama, J. Matsunaga, H. Muta, M. Uno, and S. Yamanaka, Mechanical Properties of Titanium Hydride, *J Alloys Compd.*, **381**, Nos. 1–2: 215–220 (2004);
https://doi.org/10.1016/j.jallcom.2004.04.073
149. O.M. Ivasishin, D.G. Savvakin, D.V. Oryshych, O.O. Stasiuk, and L. Yuanyuan, Hydride Approach in Blended Elemental Powder Metallurgy of Beta Titanium Alloys, *MATEC Web of Conferences*, **321**: 03009 (2020);
https://doi.org/10.1051/matecconf/202032103009
150. K. Wang and R. Reeber, High Temperature Bulk Moduli and Self-Diffusion for Tantalum and Tungsten, *High Temper. Mater. Sci.*, **36**: 185–193 (1996).
151. O.E. Dmytrenko, I.V. Kolodiy, T.B. Yanko, V.M. Borysenko, K. Irwin, and R.L. Vasilenko, Synthesis of the Ti–Zr–Ni Alloys by the "Hydride Cycle" Method, *Phys. Technol. Struct. Mater.*, **137**, No. 1: 111–121 (2022);
https://doi.org/10.46813/2022-137-111
152. V.A. Dekhtyarenko, D.G. Savvakin, O.O. Stasiuk, and D.V. Oryshych, Hydrogen Absorption and Desorption by Niobium and Tantalum, *Metallofiz. Noveishie Tekhnol.*, **44**, No. 7: 887–897 (2022);
https://doi.org/10.15407/mfint.44.07.0887

153. M.O. Vasylyev and P.O. Gurin, Structure and Properties of 3*D* Printed Zirconia Applied in Dentistry, *Prog. Phys. Met.*, **24**, No. 1: 106–131 (2023); https://doi.org/10.15407/ufm.24.01.106

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ОСТАННІ ТЕНДЕНЦІЇ В РОЗРОБЛЕННІ СПЛАВІВ НА ОСНОВІ Ti–Zr ДЛЯ БІОМЕДИЧНИХ ЗАСТОСУВАНЬ І ТЕХНОЛОГІЇ НАВОДНЕНИХ ПОРОШКІВ ДЛЯ ЇХ ВИГОТОВЛЕННЯ

Сплави на основі таких елементів, як Ti, Zr, Nb і Ta, є основними металевими біомедичними матеріалами. Правильний вибір композицій на основі цих металів забезпечує необхідну біосумісність і механічну сумісність із кісткою й іншими тканинами живого організму, досягнення високих показників міцності за достатньої корозійної стійкості в кислотних і лужних середовищах, а саме ці критерії є ключовими під час виготовлення медичних імплантатів. Зазначено переваги одержання сплавів біомедичного призначення за порошковою технологією порівняно з традиційними методами (застосування технології вакуумного лиття та гарячого деформування). Розглянуто використання Гідрогену як тимчасового легувального елементу до вказаних металів у порошкових технологіях і позитивний вплив Гідрогену на зменшення залишкової пористості під час формування сплавів з поліпшеним комплексом фізико-механічних характеристик.

Ключові слова: біосумісні матеріали, титан, цирконій, модуль Юнга, корозійна стійкість.