Structure and properties of low modulus titanium alloy Ti–26Nb–7Mo–12Zr

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The calculation of the choice of a new low modulus titanium β alloy was described. The investigations of the structure and properties (mechanical, tribological and corrosive) of low modulus titanium β alloy Ti–26Nb–7Mo–12Zr after mechanical–thermal processing were carried out. An analysis of the results of experimental research showed that the formation of homogeneous fine grained structure by sheet rolling with subsequent annealing before quenching leads to decreased elastic modulus, increased plasticity and wear resistance. Therefore, new titanium β alloy designed in the present study, Ti–26Nb–7Mo–12Zr, is expected to have good properties as biomaterial.

Keywords: Titanium β alloy, Elastic modulus, Wear test, Corrosion resistance, Biomaterials

Introduction

Nowadays, there is an increasing demand in implants made of metallic materials for various medical purposes (stomatology, orthopedics and traumatology). The actual need for implants exceeds the existing offer by three to five times on the Russian market. The main suppliers are foreign companies. The materials used for implants need an enhanced biochemical and biomechanical compatibility with a living body, an improvement of wear and corrosion resistance, strength, the ability of germination and integration with the biological environment.[1–3] In this regard, scientific research and development of technologies enabling to create the implants and materials for their production with the improved performance are actual.

Light and durable titanium alloys are the basic materials for biomedical applications because of their excellent corrosion resistance and compatibility with biological environments in comparison with other metallic biomaterials. The corrosion resistance of titanium and its alloys is significantly higher than that of stainless steel and Cr–Co alloys due to quick formation of a natural passive oxide film on their surfaces, excluding a contact with a corrosive active medium.[4] Another extremely favourable characteristic of titanium alloys used for the manufacture of implants and prostheses is their low (about twice as little than steel) modulus of elasticity, which improves the biomechanical compatibility with body tissues. From this viewpoint, titanium β alloys with elastic modulus of 60–80 GPa are the most promising. Elastic modulus of β alloys is noticeably smaller than that of α-titanium (CP-Ti) and is more popular in medicine than the two-phase ($\alpha+\beta$) type alloy Ti–6Al–4V.[1,5] Moreover, it is desirable to achieve the modulus of elasticity close to that corresponding for bone tissue (30 GPa).[6,7]

The problem of the biomechanical compatibility of implants is nowadays partially solved by development of both bulk and porous functional materials and constructions with shape memory on the basis of the intermetallic compound TiNi.[8–10] These alloys do not corrode shortly because, under passivation in a biological medium, a layer of titanium oxide containing a certain amount of nickel is formed on its surface. This is why such alloys do not possess carcinogenic and allergic activity and are widespread in medicine.[8]

Nowadays, it is generally prohibited for implants to contain toxic elements (V, Ni, Co and Cu) in their chemical composition. Taking this into consideration, the most promising is the development of nickel free low modulus titanium β alloys.

Modulus of elasticity rapidly decreases if alloying elements are correctly selected, but, as mentioned above, the toxic elements (V, Ni, Co and Cu) should be excluded. Almost ideally biocompatible metal elements are the following: Pt, Ta, Nb, Ti and Zr.[1,11,12] Alloying of these elements can lead to both an increase in the strength and a decrease in the elastic modulus, approaching the value of modulus to that of a bone tissue. The latter provides the best connection of bones with implants and its minimal damage at the bone implant junction at dynamic loadings.[1–5] In addition, a super elasticity and shape memory effect are also important for biomedical titanium alloys. These materials are Ti–Nb,[13,14] Ti–Nb–Ta,[15] Ti–Nb–Ta–Zr,[16,17] Ti–Nb–Hf–Zr[18] and Ti–Nb–Sn[19,20] system β alloys, which demonstrate the shape memory effect, depending on their thermomechanical treatment or the content of alloying elements. Importantly, very little attention has been paid to this direction of work in Russia, while the present research area is widely developed abroad.

In the present paper, we present theoretical calculations supporting a choice of alloying system and

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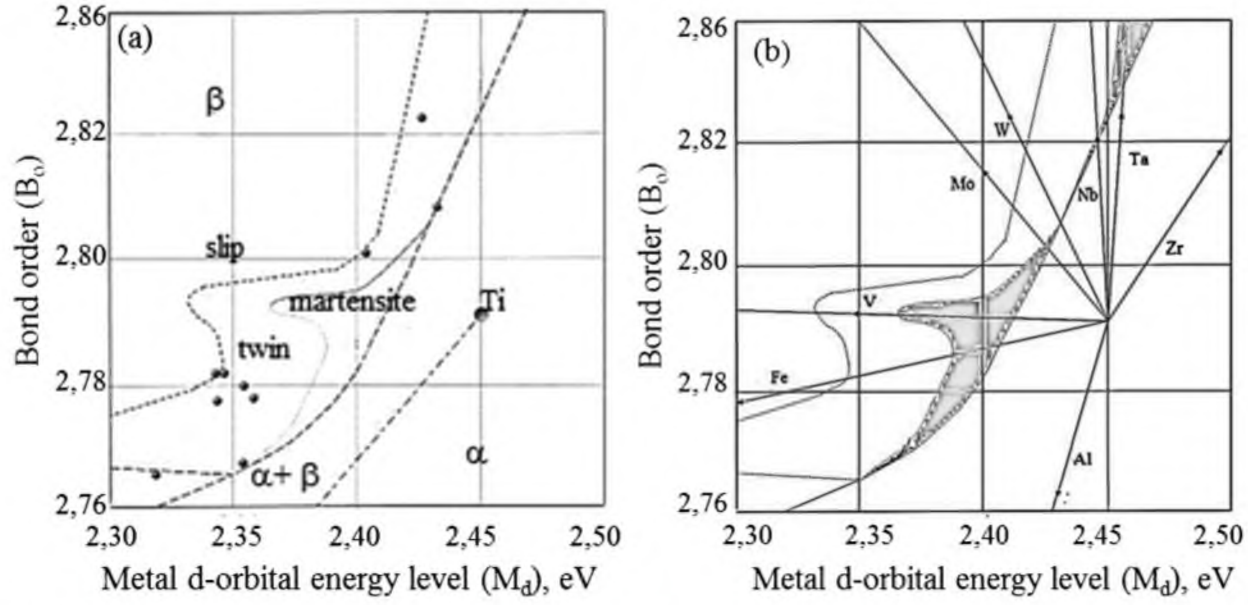


1 ***a*** **phase stability index diagram based on B_o and M_d parameters reflecting electronic structure of alloy and** ***b*** **change in phase stability (room temperature) at alloying titanium different elements [length of each vector (element of** ***X*****) corresponds to composition of compound Ti–10 at-%*X*][22]**

experimental characterisation of structural, mechanical, corrosive and tribological properties of a new low modulus titanium β alloy in comparison with coarse grained titanium alloys VT1-0 (CP-Ti grade 4) and VT6 (Ti–6Al–4V).

Experimental

A new low modulus titanium β alloy with the system of alloying Nb–Mo–Zr was developed by the authors of this paper together with Professor A. A. Zisman.[21] The approach proposed in that work[22] was used as a theoretical basis for choosing the alloying system. The electronic structure of complex alloying titanium alloy has been calculated using the published method[23] that is characterised by two parameters: a degree of the covalent bond (bond order B_o) between titanium and the alloying element and a metal d orbital energy level M_d. These parameters are given for various metallic elements in Table 1.

The effective values of the parameters B_o and M_d are defined as the corresponding weighted average for the alloys of complex composition (several elements of alloying with the given atom fraction c_i)

$$B_0 = c_1 B_{01} + c_2 B_{02} + \ldots + c_n B_{0n} \quad (1)$$

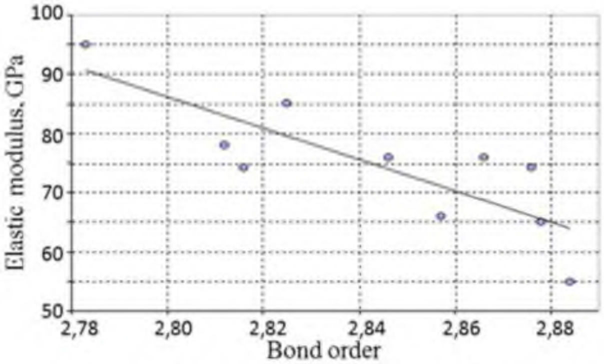
$$M_d = c_1 M_{d1} + c_2 M_{d2} + \ldots + c_n M_{dn} \quad (2)$$

Figure 1 shows a diagram of all possible compositions in the coordinates B_o–M_d adapted from a published work.[22] This diagram allows to estimate phase stability of β-titanium alloys, because the areas α, $\alpha+\beta$ and β type alloys are clearly separated. At alloying of various elements, the image point of the specific alloy moves on the diagram as it is shown on Fig. 1*b*. Each arrow responds to the titanium 10 at-% of the corresponding alloying element. Their cumulative effect can be estimated by a simple geometric summation of these vectors with their weight factors corresponding to the considered composition. However, it is recommended to use Table 1 for more accurate calculations.

According to published studies,[11,24,25] the dependence $E(B_o)$ was calculated (Fig. 2). It shows a clear tendency of decreasing elastic modulus versus increasing B_o with the desirable elasticity modulus E=65 GPa achieved in the range $2{\cdot}860 \leq B_o \leq 2{\cdot}885$. The composition of alloy must also correspond to $2{\cdot}43 \leq M_d \leq 2{\cdot}48$ for the optimal combination of the mechanical properties. These requirements are easily satisfied in the alloying titanium system by the following elements: Nb, Mo and Zr. Niobium is the reasonably inefficient stabiliser and hardener. At the same time, the use of Nb in this case is

Table 1 Values of B_o and M_d for various metallic elements

Element	B_o	M_d/eV	Element	B_o	M_d/eV	Element	B_o	M_d/eV
Ti	2·790	2·447	Nb	3·099	2·424	W	3·125	2·072
V	2·805	1·872	Mo	3·063	1·961	Re	3·061	1·490
Cr	2·779	1·478	Tc	3·026	1·294	Os	2·980	1·018
Mn	2·723	1·194	Ru	2·704	0·859	Ir	3·168	0·677
Fe	2·651	0·969	Rh	2·736	0·561	Pt	2·252	0·146
Co	2·529	0·807	Pd	2·208	0·347	Au	1·953	0·258
Ni	2·412	0·724	Ag	2·094	0·196	Al	2·426	2·200
Cu	2·114	0·567	Hf	3·110	2·975	Si	2·561	2·200
Zr	3·086	2·934	Ta	3·144	2·531	Sn	2·283	2·100



2 Relationship between elastic modulus and degree of covalent interatomic bonds in titanium β alloys

fully justified because of its special role in increasing of B_o. In addition, if it is necessary, molybdenum allows stabilising the β phase.

When a specific chemical composition of perspective medical titanium β alloys is determined on the basis of the chosen alloying system Nb–Mo–Zr, first of all, it is necessary to specify the value of a k_β, stabilisation factor for the β phase. This parameter is expressed through the critical concentrations of alloying elements p_β, each of which is equal to the minimum content (wt-%) of the stabiliser X, which helps to receive the 100% β phase in a Ti–X alloy at room temperature by its quenching from high temperature β region. The values of p_β for Nb and Mo are 37 and 11% respectively, whereas Zr does not affect k_β. The value of k_β is expressed as follows

$$k_\beta = \sum_i \frac{p_i}{(p_\beta)_i} \tag{3}$$

where p_i is content (wt-%) of the ith alloying element.

Three compositions, Ti–28Nb–7Mo–7Zr (k_β=1·39), Ti–26Nb–8Mo–12Zr (k_β=1·43) and Ti–26Nb–8Mo–14Zr (k_β=1·43), have been chosen to ensure the stabilisation coefficient $k_\beta \approx 1·4$. The alloying was carried out in the production centre of Corporation VSMPO-AVISMA (Verkhnyaya Salda, Russia). Ingots were produced by triple vacuum arc remelting and subsequent forging at temperatures above the recrystallisation temperature. As a result of primary selection, the alloy Ti–26Nb–7Mo–12Zr (the real content of elements), which showed the best homogeneity on elemental composition, has been selected for further characterisation in the present work.

The alloy Ti–26Nb–7Mo–12Zr in the form of a sheet sample with 6·7 mm thickness was subjected to sheet rolling for fine grained structure formation. Sheet rolling was carried out without heating at room temperature with a reduction of 100–200 μm in one pass with total strain of 90%. The deformed specimens after rolling were annealed at 850°C and then quenched in water.

We carried out structural studies using an optical microscope Olympus 71 and a scanning electron microscope Quanta 600 FEG with a field emission gun. Investigation of the structural phase state and the crystallographic texture was also performed using a method of automatic analysis of the electron backscattered diffraction pattern on the scanning electron microscope Quanta 600 FEG for the accelerating voltage of 20 kV and beam current of 13 nA by software TexSEM Lab (TSL).

Specimens for the above stated methods were cut using an electrical discharge machine and then went through mechanical grinding on a device TegraPol-31 firm 'Struers'. Surface of the samples was prepared for optical metallography by chemical etching in 4 mL HF+6 mL HNO_3+190 mL H_2O solution. For scanning electron microscopy, samples were electropolished using a device LectroPol-5 (Struers) with 60 mL $HClO_4$+600 mL CH_3OH+360 mL $CH_3(CH_2)$ $CH_2OCH_2CH_2OH$ solution at voltage U=50 V.

Mechanical tensile strength tests were carried out on a universal electromechanical testing machine Instron 5882 with a strain rate of 1·5 mm min^{-1}. The testpieces were cut with an electrosparking machine in the form of double blades with working part sizing as 3×4×38 mm. Further, the surface of the samples went through mechanical grinding. According to the results of tests, the elastic modulus E, yield strength $\sigma_{0·2}$, ultimate tensile strength and total elongation (TE) were evaluated. Modulus of elasticity was evaluated from the slope of the elastic part of the stress–strain curve.

The wear tests were carried out on an automated friction machine (High-Temperature Tribometer; CSM Instruments, Switzerland) according to the test scheme 'ball disc'. We have chosen the ball of steel 100Cr6 with a diameter of 6 mm as a rider. The experiment was carried out in the mode of dry friction in air. The wear characteristics were determined at a load of 2 N on the rider, with the rotation speed of the sample at 10 cm s^{-1} and sliding distance of 200 m. The wear rate of the sample and rider was estimated immediately after the test from the value of wear factor, calculated by the following formula

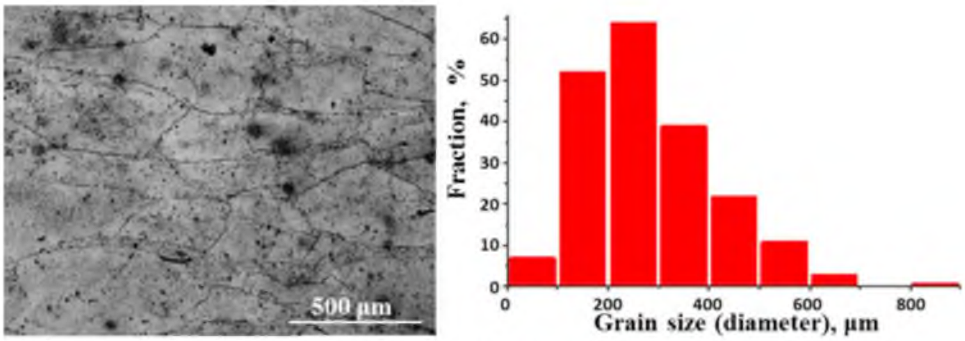
$$W = \frac{V}{Pl} \tag{4}$$

where W is the factor of wear (mm^3 N^{-1} m^{-1}), V is the volume of loss of the material (mm^3), P is the load (N) and l is the length of friction (m).[26]

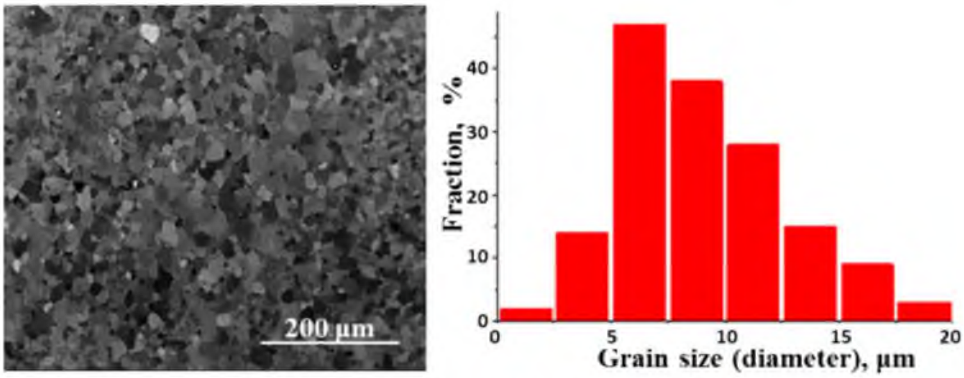
Corrosion resistance of the alloy was studied in a 1% aqueous solution of NaCl (Ringer solution) at room temperature. Each of the samples was kept in the etching solution not <3 h to achieve the value of the stationary potential before an anodic polarisation. The potential change should not exceed 30 mV in the last 0·5 h (GOST 9·912-89). The anodic polarisation tests were carried out by a potentiodynamic method using a silver chloride electrode for comparison. The anodic polarisation curves are built using the given values of the potential and

Table 2 Chemical composition of titanium alloys VT1-0 and VT6

	Content of elements (Ti base)/wt-%									
Alloy	Al	Mo	V	Zr	Fe	Si	O_2	C	N_2	H_2
VT1-0	0·01	...	...	...	0·12	0·002	0·143	0·004	0·003	0·0008
VT6	6·46	...	3·84	0·02	0·083	0·010	0·166	0·005	0·003	0·003



3 **Microstructure (optical metallography) and histogram of grain size for Ti–26Nb–7Mo–12Zr alloy**



4 **Image (SEM) of microstructure and histogram of grain size for Ti–26Nb–7Mo–12Zr alloy after its rolling at 90% reduction and subsequent annealing at *T*=850°C before quenching**

obtained values of an anode current, and the electrochemical characteristics of the samples were determined.

Unalloyed titanium VT1-0 and alloy VT6 (the content of impurity in VT1-0, which was produced in Corporation VSMPO-AVISMA, and the chemical composition of alloy VT6 are shown in Table 2) with an average grain size of 6 and 8 μm respectively were used to compare the wear and corrosion properties with the low modulus titanium β alloy.

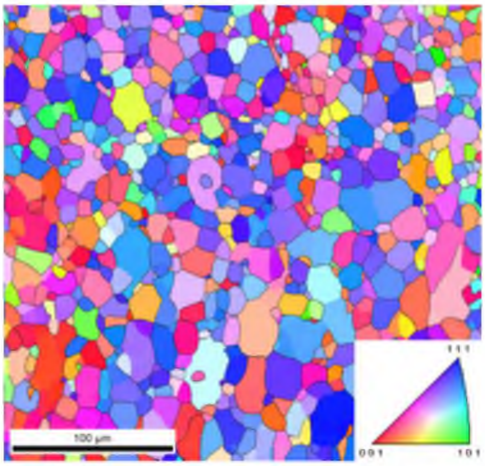
Results and discussion

The investigated forged ingot of the titanium β alloy Ti–26Nb–7Mo–12Zr in the initial state presented a fully β phase with an average grain size of ~280 μm (Fig. 3).

As a result of sheet rolling with subsequent annealing before quenching, homogeneous fine grained state was formed in the Ti–26Nb–7Mo–12Zr alloy (Figs. 4 and 5). The average grain size, defined by a linear intercept method, as it can be seen from the presented histogram of grain size in Fig. 4, is about 9 μm. In this case, the presented microstructure is characterised by inequigranular. This is probably due to the fact that the nucleation of grains during the initial stages occurs at the grain boundaries and further in the volume of deformed grains.

According to the analysis of electron backscattered diffraction pattern patterns, it was found that the volume of high angle grain boundaries in the alloy with its fully recrystallised fine grained structure is ~80% (Fig. 5).

Measurement of elastic modulus by mechanical tensile tests of the alloy samples has shown that its value in the initial state is 84 GPa. As a result of cold rolling and subsequent annealing, its elastic modulus decreases to



5 **Map of crystallographic orientations (high angle grain boundaries are identified by black marker) in Ti–26Nb–7Mo–12Zr alloy after its rolling at 90% reduction and subsequent annealing at *T*=850°C before quenching**

Table 3 Mechanical properties of Ti–26Nb–7Mo–12Zr alloy*

Ti–26Nb–7Mo–12Zr	*E*/GPa	$\sigma_{0\cdot2}$/MPa	UTS/MPa	TE/%
Coarse grained state	83·7±0·2	793±5	800±6	6·3±0·2
Homogeneous globular structure (average grain size ~9 μm)	66·6±1·4	754±7	759±7	8·5±1·2

*UTS: ultimate tensile strength; TE: total elongation.

66 GPa (Table 3). As it can be seen from the data in the table, the strength characteristics were slightly decreased upon mechanical–thermal treatment, while the TE was increased by 2% in comparison to the initial state. However, a Hall–Petch relationship was not carried out for a given alloy. This is probably connected with an anisotropy of the strength properties in the initial state.

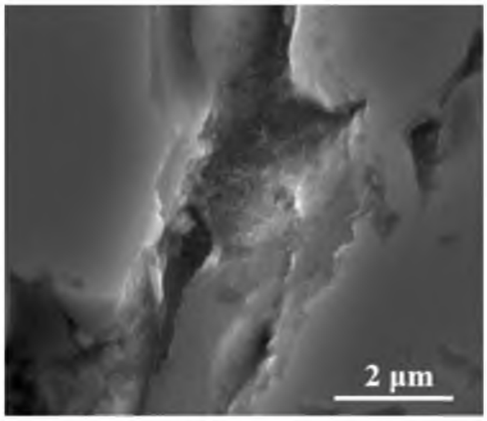
It is known that wear is a critical process in use of implant, which determines its lifetime in a living organism. Low wear resistance of an implanted material can lead to various adverse consequences for a living organism. It is interesting to note that titanium and its alloys have low tribological characteristics in pairs 'metal–metal' due to the high propensity to frictional seizure. This phenomenon is promoted by low values of the elastic modulus and the low thermal conductivity.[27]

Table 4 shows the wear factor values obtained at wear tests for the samples of the investigated alloy and rider. The analogous studies of unalloyed titanium VT1-0 and industrial alloy VT6, which is widely used for the manufacturing medical implants, were conducted for comparison with the new low modulus Ti–26Nb–7Mo–12Zr alloy. These studies have shown the higher values of wear resistance for the low modulus titanium β alloy as compared to VT1-0 and VT6. The wear factor of unalloyed titanium VT1-0 and alloy VT6 more than two times exceeds the corresponding values for the investigated alloy. This is probably connected with a high content of niobium in this alloy. The addition of this element in titanium alloys leads to quick passivation of the alloy surface, and the resulting oxide of niobium (Nb_2O_5) possesses good lubricating properties according to the published data.[6]

It is interesting to note that a coarse grained Ti–26Nb–7Mo–12Zr β alloy in its initial state exhibits high wear resistance as compared to the homogeneous fine grained structure formed as the result of mechanical–thermal treatment.

The β type titanium alloy as well as α type and $(\alpha+\beta)$ type titanium alloys, widely used in medicine, demonstrated high corrosion resistance. However, this alloy possesses high corrosion resistance as compared to the corresponding data obtained for VT1-0 (Table 5). This is probably due to the fact that the oxides of alloying elements, especially Nb and Zr, which formed on the surface of the alloy, according to published works,[6,28–30] increase the corrosion resistance of titanium alloys.

Surface studies by scanning electron microscopy has shown that all studied states of the alloy Ti–26Nb–7Mo–12Zr are characterised by deep spot destructions after anodic polarisation. These destructions testify about that occurred in a pitting corrosion (Fig. 6) (GOST 9·908-85). It is known that the development of the pitting corrosion is promoted by various defects of structural and structural inhomogeneities, such as grain boundaries and subgrains, dislocation cluster, secondary dispersed separation and phase.



6 Image (SEM) of Ti–26Nb–7Mo–12Zr alloy surface after its anodic polarisation in state after rolling at reduction 90% and subsequent annealing at T=850°C before quenching

The corrosion resistance of the investigated alloy was estimated by comparing the anode current density in the passive area, the pitting potential and stationary potential (Table 5). The pitting potential characterises the damage of a passive layer and is the least one at which the process of pitting begins. The obtained potential and corrosion current density values for the alloy Ti–26Nb–7Mo–12Zr vary in a small range, and such small changes are not the sufficient criterion of corrosion resistance in this case. However, the values of the potentials for the investigated alloy are significantly higher than for unalloyed titanium VT1-0.

Conclusions

In the present work, the new low modulus titanium β alloy Ti–26Nb–7Mo–12Zr was investigated and characterised. The formation of the homogeneous globular structure with an average grain size of $\sim$9 μm leads to the significant decrease in its elastic modulus from 84 to 66 GPa as compared to the initial state with the average grain size of 280 μm.

Table 4 Wear factor of Ti–26Nb–7Mo–12Zr alloy and rider

	Ti–26Nb–7Mo–12Zr			
	Coarse grained state	Homogeneous globular structure (average grain size $\sim$9 μm)	VT1-0	VT6
Wear factor/ $\times 10^{-4}$ mm^3 N^{-1} m^{-1}	1·8	2·1	4·3	5·3
Wear factor of rider/ $\times 10^{-5}$ mm^3 N^{-1} m^{-1}	1·4	1·2	2·0	2·4

Table 5 Electrochemical characteristics of Ti–26Nb–7Mo–12Zr alloy (data are given relative to silver chloride electrode, stationary potential is 201 mV)

	Ti–26Nb–7Mo–12Zr		
	Coarse grained state	Homogeneous globular structure (average grain size $\sim$9 μm)	VT1-0
Stationary potential/mV	−187	−158	−242
Pitting potential/mV	1480	1495	−150
Corrosion current density/mA cm^{-2}	0·007	0·006	0·01

The alloy Ti–26Nb–7Mo–12Zr is less subjected to wear (the wear factor of the coarse grained state with an average grain size of $\sim$280 μm is $1{\cdot}8\times10^{-4}$ mm^3 N^{-1} m^{-1}, the wear factor of the fine grained state with an average grain size of $\sim$9 μm is $2{\cdot}1\times10^{-4}$ mm^3 N^{-1} m^{-1}) in comparison with the α-titanium (VT1-0) (the wear factor is $4{\cdot}3\times10^{-4}$ mm^3 N^{-1} m^{-1}) and $(\alpha+\beta)$ alloy VT6 (the wear factor is $5{\cdot}3\times10^{-4}$ mm^3 N^{-1} m^{-1}) widely used in medicine. The corrosion resistance of the alloy Ti–26Nb–7Mo–12Zr was much higher than that of CP-Ti (VT1-0). This is most favourable for material used in implantology.

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