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ZIRCONIUM MATERIALS FOR MEDICAL APPLICATIONS

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The peculiarities of production nanostructured alloy Zr1%Nb using deformation methods for medical implants and their basic properties are investigated. The changes of the morphology, structure and properties of the oxide coatings on the surfaces of Zr1%Nb alloy formed in air at 500…800 ºC for a time up to 10 h are analyzed. Biocompatibility zirconium oxide coatings can be applied to the surfaces of orthopedic implants in bone surgery and dentistry and for the manufacturing of surgical instruments.

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INTRODUCTION

Metallic biomaterials are mainly used for replacing failed hard tissue. Implant materials must combine high strength, corrosion resistance and tissue compatibility. The longevity of the implant is of prime importance especially if the recipient of the implant is relatively young because it is desirable that the implant function for the complete lifetime of a patient. Because certain metal alloys have the required mechanical strength and biocompatibility, they are ideal candidates for the fabrication of prostheses. These alloys include stainless steels, chrome-cobalt-molybdenum alloys and titanium alloys.

The selection of a biomaterial depends on its specific medical application. In order to serve safely and appropriately for a long period of time without rejection, a metallic implant should possess the following essential characteristics, but not limited to: excellent biocompatibility (non-toxic); high corrosion resistance; suitable mechanical properties; high wear resistance; Osseo-integration (in the case of bone prosthetics) [1].

Recently, titanium alloys are getting much attention for biomaterials. The use of titanium alloys as biomaterials has been increasing, due to their biocompatibility and enhanced corrosion resistance compared to stainless steels and cobalt based alloys. The α-β alloy Ti-6Al-4V is the most widely used titanium alloy. However, there is toxicity of alloying elements and lack of mechanical biocompatibility of conventional titanium alloy Ti-6Al-4V [2]. The release of metal ions from titanium alloy implants may generate an adverse biological effect or elicit allergic reactions. Vanadium and aluminum in the Ti-6Al-4V alloy were shown to be potentially cytotoxic, and, over time, the alloy produced adverse reactions in the body tissues [3]. The excellent corrosion resistance of zirconium has been known for many years. Zirconium displays excellent corrosion resistance in many aqueous and non-aqueous media and for this reason has seen an increased use in the chemical process industry and in medical applications [4]. When zirconium is exposed to an oxygen-containing environment, a protective oxide film spontaneously forms on its surface, in both dry and wet conditions. Moreover, this film is self-healing and protects the base metal from chemical attack at temperatures up to 300 °C. As a result, zirconium is very resistant to corrosive attack in most mineral and organic acids, strong alkalis and saline solutions [1]. A limitation to the wider application of zirconium in these areas is its relatively low resistance to abrasion and its tendency to gall. This relatively low resistance to abrasion and the tendency to gall is also demonstrated in zirconium alloys.

Zirconium metal exhibits the highest biocompatibility of all metals in the humans body (Fig. 1), and zirconium compounds are of low toxicity [1].

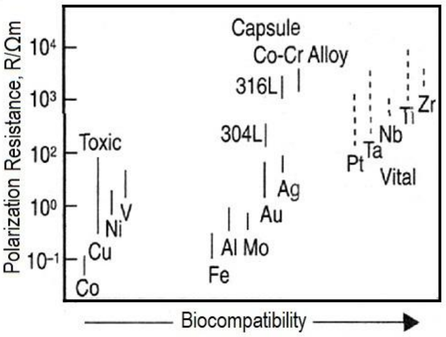


Fig. 1. The relationship between polarization resistance and biocompatibility of pure metals, cobalt-chromium alloy and stainless steels [5]

Zirconium and zirconium alloys are the most inert metals relative to biological environments, and this property allows the use of them for the fabrication of implants in bone surgery and dentistry, as well as for the manufacturing of surgical instruments. However, during long-term functioning of the implant in the human body due to the electrochemical reaction of the biological environment with it, the surface working layers of the implant begin to corrode. This provokes the occurrence of metallosis, inflammation of tissues around the implant and secondary infection. Therefore, as a rule, one of the main elements of the process of manufacturing such implants is the formation of a long-term bioinert coating on them surfaces. Oxidation in high temperature air transforms the metallic zirconium alloy surface into a stable, durable, low-friction oxide ceramic without creating the risk for brittle fracture associated with monolithic ceramic components [6, 7].

The use of zirconium after casting, which has a coarse-grained structure for the fabrication of implants, gives zirconium workpieces brittleness and creates problems during their mechanical processing, in particular, when polishing the working surfaces of the implant. The zirconium or zirconium alloy workpieces must have a finely dispersed microstructure with strong intercrystalline bonds which will improve the conditions of them mechanical processing and increases strength. The formation of bioprotective zirconium oxide coatings on the implant provides a barrier between the metallic prosthesis and body tissue thereby preventing the release of metal ions and corrosion of the implant.

Despite progress in the use of zirconium materials in medicine, insufficient attention has been paid to the study of their processing technologies for use in traumatology and orthopedics. The aim of the work is to obtain a nanostructured zirconium alloy and study the oxidation kinetics, surface structure and mechanical properties of zirconium oxide coatings formed on Zr1%Nb alloy samples.

MATERIALS AND EXPERIMENTAL PROCEDURES

The initial material for nanostructured zirconium materials obtained was zirconium and Zr1%Nb alloy ingots. The chemical composition of the alloy ingots is presented in Table 1. Ingots were checked for internal defects by ultrasonic method using a UD-270 device with a set of emitters, which allows detecting defects as small as 100 μm.

Table 1

The content of impurities in zirconium ingots, wt.%

Element	N	C	O	Fe	Si	Ni	Ti
wt.%	0.006	0.016	0.14	0.03	0.01	0.01	0.001
Element	Al	Ca	Cr	Mn	Hf	Nb	Zr
wt.%	0.003	0.03	0.001	0.0005	0.024	1.0	98.7

For production of a fine dispersion structure of zirconium alloys hot forging of ingots to wrought barstock was used. Ingots for forging were heated in a furnace to a temperature of 850 °C and then forged using a pneumatic air forging hammer MA4136. After machining the wrought barstocks, subsequent deformation was carried out on a rolling mill in shaped rolls at room temperature. The maximum percentage of deformation did not exceed 45%. After rolling zirconium or zirconium alloy was then subjected to an abrasive surface preparation process by centerless grinding machine. The abrasive surface preparation process was used to induce an altered surface roughness (R_a). The appropriate altered surface roughness is induced by altering the pre-existing surface roughness to an altered surface roughness of such a magnitude as alloy, each having a fined microstructure and an appropriately altered surface roughness, is subjected to an oxidation process. After such processing, bars with diameters of 16...30 mm and a length of 300...500 mm were obtained.

The obtained bars samples then were subjected to process conditions which cause the natural (in situ) formation of a tightly adhered, diffusion-bonded coating of uniformly thick zirconium oxide on their surface. The process conditions include air oxidation. This process ideally provide a hard, dense, blue-black or black, low-friction wear-resistant uniformly thick zirconium oxide film or coating of thicknesses typically on the order of several microns on the surface of the samples. Below this coating, diffused oxygen from the oxidation process increases the hardness and strength of the underlying substrate metal.

Zirconium bars samples were placed in a furnace having oxygen containing atmosphere (such as air) and typically heated at 500…800 °C for from several minutes up to about 10 h. However, other combinations of temperature and time are possible. When higher temperatures were employed, the oxidation time were reduced to avoid the formation of the white oxide.

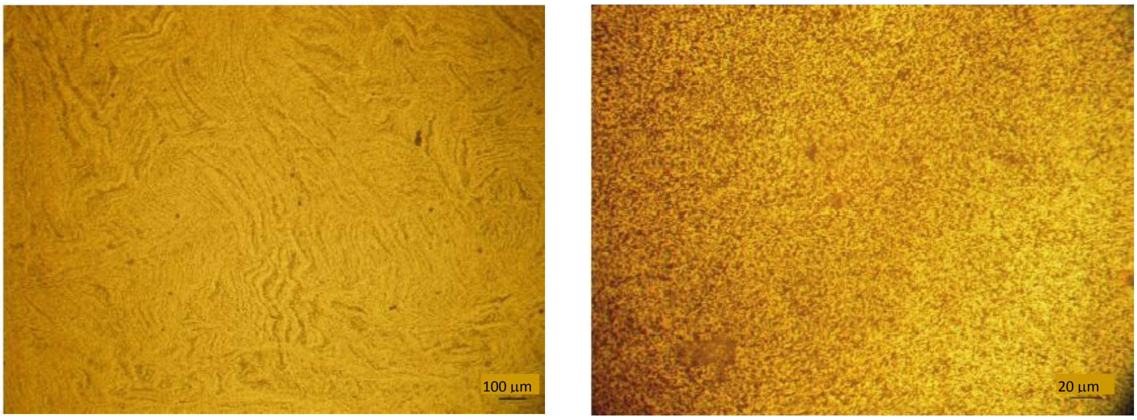
The structure and microhardness of the samples were studied in the longitudinal and transverse sections of the resulting bars. The microstructure of the samples was studied by the standard metallographic method on an MMP-4 optical microscope. The microhardness (H_μ) measurements were made using a PMT-3 device; the load used was 0.1 kg. The Brinell hardness (HB) measurements were made using a TSh-2 device; the load used was 100 kg. Studies of the mechanical properties of zirconium rods were carried out on the installation Instron-5581 at a temperature of 20 °C.

The surface structure of the obtained coating and their elemental composition were investigated by the autoemission scanning electron microscope JSM-7001F with energy dispersive microanalysis system INCA Energy 350. The thickness of the oxide coating on the oxidized samples was determined by fractography images of the fractures using a scanning electron microscope FEI Quanta 600 FEG.

To measure the roughness parameters of the surface of samples the portable profilometer-profilograph TR200 production of the company Time Group Inc was used by which the magnitude of R_a (average arithmetic roughness surface according to international standard ISO 4287) was determined.

EXPERIMENTAL RESULTS AND DISCUSSION

The microstructure was analyzed at each processing steps. The microstructure of the studied alloys after hot forge and rolling are given in Fig. 2. The structure obtained during the forge process is heterogeneous (see Fig. 2,a). The structure of zirconium alloy after rolling is homogeneous fine (see Fig. 2,b) and an acceptable degree of fine microstructure for formation of a tightly adhered, diffusion-bonded coating of uniformly thick zirconium oxide on its surface. Microstructural analysis showed that as a result of the application of free forge at high temperature and hot rolling, bars of zirconium alloys were obtained in a finely dispersed (nanostructured) state.



a *b*

Fig. 2. The microstructure of the Zr1%Nb alloy after hot forge (a) and rolling (b) in transverse section of the resulting bars

The tested values of microhardnes and Brinell hardness of the zirconium alloy after various processing are tabulated in Table 2. Comparing the values of hardness of the obtained bars is observed increasing the values of hardness for alloys after hot forge and rolling.

Recrystallization annealing of the obtained zirconium bars was carried out to relieve internal stresses arised during machining. Recrystallization annealing was carried out without structural change, while the values of microhardness and hardness decreased as shown in Table 2.

The mechanical properties of the resulting zirconium rods, as well as for comparison, data for titanium alloys, are given in Table 3. A comparative analysis of these data shows that according to the indicated parameters, the zirconium alloy meets the requirements of the ISO 5832 standard (Implants for surgery – Metallic materials) and has higher physical and mechanical properties than some titanium alloys. The obtained results indicate that the use of a zirconium alloy with special mechanical and thermal treatment, in comparison with traditional titanium alloys, makes it possible to obtain structural elements with a predominantly higher level of mechanical properties responsible for the operational durability of the products.

Table 2

Comparison of results of measurement the values of hardness

Hardness, MPa	Values of hardness of Zr1%Nb		
	Hot forging	Hot forging and rolling	Annealing
H_μ	2100	2360	2210
HB	2500	2770	2090

Table 3

The mechanical properties of the resulting Zr1%Nb rods.
In the last columns the data for the titanium alloys is given for comparison

Property	Zr1%Nb		BT-1-0*	BT-6**
	After deformation	After annealing		
Ultimate tensile strength, MPa	910…920	630…670	355…540	860
Yield strength, MPa	630…420	340…390	–	780

*GOST 26492-85; **ISO 5832-3

Creation of a uniform oxide coating during the oxidation process is dependent on both a surface with appropriate surface roughness and a microstructure with sufficient refinement. The oxide coating initiates and grows from surface asperities, so the oxide initiation sites may be spaced too far apart to produce a uniform coating thickness on a Surface that is too smooth. The oxide layer grows by oxygen diffusion along grain boundaries and through microstructural grains. The oxidation rate can be different in grains of different Structure and composition (such as between alpha and beta grains in a two-phase zirconium alloy). Thus, the oxide coating may not grow with a uniform thickness through a microstructure that is too coarse. Specific limits for the necessary minimum surface roughness and maximum microstructural refinement can be alloy and application dependent.

To determine the regularities of zirconium oxide coating formation due to thermal influence the electron microscopic studies on the oxidized samples have been made.

At complex study of functional oxide coatings on zirconium materials it has been found temperature effect of air-thermal oxidation on morphology and composition of the modified surfaces. At temperature up to 600 °C durable blue-black oxide coatings of uniform structure is formed on the surface of the zirconium alloy. Further increase of temperature to 800 °C leads to an increase in the oxygen content and the oxide coating growth (Table 4). With increasing thick of the oxide coating the mechanical stresses at the border oxide-metal are increased and therefore a sharp change in corrosion resistance is observed [8]. Long-term oxidation times and higher oxidation temperatures violate the coating integrity. Formation of cracks and destruction of the oxide coating occurs.

The chemical composition has a significant impact on the structure of the oxide coating too [9]. The composition of oxide coating affects on their mechanical and protective properties since a dense solid oxide coating can protect the metal from further oxidation. In the study of the oxidation process it was found that for pure zirconium and zirconium doped with niobium onset temperature of cracking of the oxide film is different [9]. All samples had continuous glossy coating after annealing at 500…600 °C. An inhomogeneous structure with some separation into fragments are formed or Zr1%Nb alloy at 800 °C while for pure zirconium cracks are clearly visible due to the formation of smaller amounts of the tetragonal phase in the oxide layer. Due to the low volume fraction of tetragonal oxide a fracture toughness of the oxide coating becomes much lower therefore the oxide layer is susceptible to microcracks and loses its protective structure [10]. The structure of Zr1%Nb alloy after oxidation has a significant amount of a white tetragonal phase so the formation of cracks in the oxide layer occurs not as intensively as in the case of pure zirconium.

The thickness of oxide coating formed on the Zr1%Nb alloy surface at 800 °C almost 2 times less than the thickness of the coating (84.18 μm) on pure zirconium. This fact is explained by the presence in the alloy of niobium which stabilizes the corrosion resistance of undoped zirconium that is eliminates the adverse effect of small amounts of impurities present in pure zirconium [11]. It is known that the doping of zirconium may significantly reduce the oxidation rate [8].

The minimum oxide coating thickness which is necessary for the protection and stabilization of metal corrosion process depends on many factors: temperature, chemical composition and structure, the manufacturing process and preparation of the sample surface, etc. Studies oxidation kinetics of zirconium materials have shown that increase oxidation times will increase the weight gain of sample and significantly depends on temperature (see Table 4). Longer oxidation times and higher oxidation temperatures will increase oxide coating thickness, but may compromise coating integrity.

Oxidation kinetics behavior basically refers to the variation of oxidation rate with time. Corrosion behavior of zirconium materials is determined by properties of the barrier oxide coating. The growth of the oxide coating under isothermal conditions in the temperature range studied is not subject to any one law and cannot be described by one kinetic equation. At certain temperatures the transition from one to another oxidation law is observed. In the oxidation of zirconium materials there are several stages [8, 12, 13].

The growth of the oxide coating on a Zr1%Nb alloy surface in the temperature range 500…600 °C occurs according to a parabolic or cubic law up to oxide thickness of 2…3 μm. The inner part of the coating is nonstoichiometric, the outer part is close to the stoichiometric composition. Such oxide coating is an effective protective barrier for oxidation. According to a parabolic law, the rate of the oxidation process is inversely proportional to the thickness of the oxide coating. This law applies when on the metal surface during its oxidation the coating which has protective properties is formed, i.e. it is solid and nonporous.

Oxidation kinetics is replaced by quasilinear when further growth of the oxide coating thickness more than 3 μm. The corrosion rate increases sharply at temperatures above 700 °C. This oxidation stage is characterized by fast oxidation and a number of oxide coating defects such as cracks and pores (Fig. 3). Transition from the protective oxide coating to the flake it off occurs for relatively short time after which Zr1%Nb alloy are oxidized with increased rate to complete destruction.

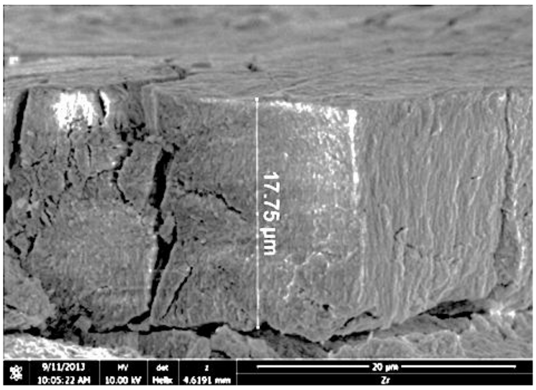


Fig. 3. Fractography images of the fracture of the coating formed on Zr1%Nb alloy at 700 °C

Roughness parameter R_a of the oxide coating formed at temperatures up to 600 °C is not more than 0.1 μm. When tested of zirconium materials in more severe conditions (higher temperature) a thicker oxide coating is formed, roughness is increased.

Table 4

Characteristics of oxide coatings formed on Zr1%Nb alloy samples

Temperature, °C	600	700	800
Oxidation time, h	8	10	8
Oxygen content, wt.%	23.13	24.5	26.17
Weight gain (Δm), mg	4.4	15.95	51.7
Roughness (R_a), μm	0.100	0.632	1.848
Thickness (h), μm	2.2	17.75	47.75
Microhardness (H_μ), MPa	5190	8240	8350

The value of Brinell hardness for the samples Zr1%Nb alloy is increased to 2770 MPa for all samples after oxidation. The microhardness values of the samples after oxidation at different temperatures of heating and times of annealing are significantly different. The measurement results show that with rising temperature microhardness is increased. The microhardness values for zirconium alloy as well as the results of determining the amount of oxygen, weight gain, roughness and thickness of the samples are shown in Table 4.

Thus the choice of optimal temperature and time of oxidation allows creating on the surface of zirconium materials the dense oxide coating. The protective oxide coating of a certain thickness and perfect structure (no cracks, pores) on the surface of Zr1%Nb alloy prevents further penetration of the corrosive environment in the deeper layers and therefore protects the metal from further destruction.

CONCLUSIONS

The peculiarities of production nanostructured alloy Zr1%Nb using methods of hot forging and rolling for medical implants were investigated. Basic properties of this material were studied.

The influence of the air-thermal oxidation temperature on the micromorphology, structure, and composition of the modified surfaces of the Zr1%Nb alloy has been studied. It has been established that at a temperature of 500...600 °C coatings are formed that are characterized by high strength and density. The thickness of such coatings is 2...7 μm, the roughness parameter R_a is not more than 0.1 μm. Longer oxidation times and higher oxidation temperatures will increase this thickness, but may compromise coating integrity. If the oxidation is continued to excess, the coating will whiten and separate from the metal substrate.

These diffusion-bonded, low frictions, highly wear resistant, uniformly thick blue-black zirconium oxide coatings can be applied to the surfaces of orthopedic implants subject to conditions of wear and to prosthetic implants and devices requiring a biocompatible surface.

REFERENCES

1. Q. Chen, G. A.Thouas. Metallic implant biomaterials // *Materials Science and Engineering R 87*. 2015, v. 87, p. 1-57; http://dx.doi.org/10.1016/j.mser.2014.10.001

2. T. Kodama. Study on Biocompatibility of Titanium Alloys // *J. Stomatol. Soc. Jpn*. 1989, v. 56, issue 2, p. 263-288; https://doi.org/10.5357/koubyou.56.263

3. Y. Okazaki, S. Rao, S. Asao, T. Tateishi, S. Katsuda, Y. Furuki. Effects of Ti, Al and V Concentrations on Cell Viability // *Materials Transactions, JIM*. 1998, v. 39, issue 10, p. 1053-1062; https://doi.org/10.2320/matertrans1989.39.1053

4. V.V. Luk'yanchenko, M.G. Malyasova. Metals in implantology // *Orthopaedics, traumatology and prosthetics*. 2010, N 3, p. 130-132.

5. M. Niinomi. Recent titanium R&D for biomedical applications in Japan // *J. Miner. Met. Mater. Soc.* 1999, v. 51, p. 32-34; https://doi.org/10.1007/s11837-999-0091-x

6. R.S. Laskin. An Oxidized Zr Ceramic Surfaced Femoral Component for Total Knee Arthroplasty // *Clinical Orthopaedics and Related Research*. 2003, v. 416, p. 191-196; https://doi: 10.1097/01.blo.0000093003.90435.1f

7. J.A. Davidson. Characteristics of Metal and Ceramic Total Hip Bearing Surfaces and Their Effect on Long-Term Ultra High Molecular Weight Polyethylene Wear // *Clinical Orthopaedics and Related Research*. 1993, v. 294, p. 361-378.

8. B.G. Parfenov, V.V. Gerasimov, G.I. Venediktova. *Corrosion of Zirconium and its Alloys*. M.: “Atomizdat”, 1967, 260 p.

9. M.M. Pylypenko, A.A. Drobyshevskaya, Yu.S. Stadnik, I.G. Tantsyura. Air-thermal oxidation of zirconium materials // *Problems of Atomic Science and Technology (PAST).* 2014, N 2(90), p. 103-106.

10. M.M. Pylypenko. Effect of fluoride on susceptibility of the Zr-Nb alloys to high temperature oxidation // *PAST*. 2011, N 6(76), p. 18-23.

11. A.S. Zaymovsky, A.V. Nikulina, N.G. Reshetnikov. *Zirconium alloys in nuclear technology*. M.: “Energoatomizdat”, 1994, 453 p.

12. R.F. Voytovich. *Okisleniye tsirkoniya i yego splavov*. Kyiv: “Naukova dumka”, 1989, 288 p. (in Russian)

13. V. Trush, M. Pylypenko, P. Stoev, M. Tikhonovsky, I. Pohrelyuk, V. Fedirko, A. Luk’yanenko, S. Lavrys. Influence of interstitial elements (oxygen, nitrogen) on properties of zirconium alloys (review) // *Physics and Chemistry of Solid State*. 2022, v. 23, N 2, p. 401-415; https://doi.org/10.15330/pcss.23.2.401-415

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ЦИРКОНІЄВІ МАТЕРІАЛИ ДЛЯ МЕДИЧНИХ ЗАСТОСУВАНЬ

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Досліджено особливості одержання наноструктурного сплаву Zr1%Nb деформаційними методами для медичних імплантатів та їх основні властивості. Проаналізовано зміни морфології, структури та властивостей оксидних покриттів на поверхні сплаву Zr1%Nb, сформованих на повітрі при 500…800 ºC. Біосумісні покриття з оксиду цирконію можна наносити на поверхні ортопедичних імплантатів у кістковій хірургії та стоматології, а також для виготовлення хірургічних інструментів.