Structure and properties of titanium β-alloys Ti-Nb-Mo-Zr of medical purpose

O A Golosova¹, T N Vershinina¹, M B Ivanov¹, Yu R Kolobov¹, E S Pigorev¹ and A A Zisman²

¹Research Education and Innovative Centre “Nanostructured Materials and Nanotechnologies”, Belgorod State University, Belgorod, Russia
²CRISM “Prometey”, St. Peterburg, Russia

E-mail: Ollilac@rambler.ru

Abstract. Low-modulus titanium β-alloy Ti-26Nb-7Mo-12Zr for medical application, composed of nontoxic elements V and Al was considered. The influence of deformation in combination with heat treatment on the structure and properties of β-alloys such as elastic modulus, yield strength and tensile strength, ductility was investigated.

1. Introduction
There is an increasing demand in implants made of metallic materials for various purposes in modern medicine in recent years. At the implantation of any biomaterial there is its direct contact with the tissues and media of the human body. Because of this type of materials should have certain properties. They have to provide not only mechanical and chemical biocompatibility, but wear and corrosion resistance, strength, the ability of germination and integration with the biological environment [1]. One of the most important characteristics of medical alloys is the elastic modulus, which determines the functional reliability of implants in an actual operating conditions in a human body. The value of the elastic modulus should be close to the elastic modulus of bone (30 GPa). It allows to redistribute a significant part of loads on the bone. This corresponds to normal physiological conditions and prevents premature degradation of the bone material [2].

It is believed that the best material for the production of implants are light and durable titanium alloys because of their unique corrosion resistance and biocompatibility [1, 3]. When using titanium alloys for the manufacture of implants and prostheses the extremely favorable factor is their low (approximately two times less than steel) modulus of elasticity [4]. Titanium β-alloys with elastic modulus 60-80 GPa are the most promising from this viewpoint. Elastic modulus of β-alloys is noticeably smaller then that of α-titanium (109 GPa) and most widespread in medicine two-phase (α+β)-type Ti-6Al-4V alloy. Modulus of elasticity of the most rapidly decreasing with correct selection of alloying elements, but they should not contain toxic elements (V, Al, Ni, Co et. al. [5 - 7]). These elements render allergic effect on living tissue or general toxic effect on the human body. Almost ideally biocompatible metal elements are as follows: Pt, Ta, Nb, Ti and Zr [7 - 9]. Alloying of these elements can lead to a decrease in elastic modulus and an increase in the strength of titanium, which provides the best connection to bone and minimal damage at the junction of the bone-implant [4].
In this regard, formerly authors have chosen a system of alloying of niobium, molybdenum and zirconium for the new biomedical β-type titanium alloys.

2. Materials and experimental procedures
In the present work titanium β-alloy Ti-26Nb-7Mo-12Zr in the initial state with an average size of β-grains of 280 microns in the form of a sheet sample of thickness 6.7 mm was investigated. Melting of titanium β-alloy Ti-26Nb-7Mo-12Zr was carried out by triple vacuum arc remelting in Corporation VSMPO-AVISMA (Verkhnaya Salda, Russia).

Low-modulus titanium β-alloy 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 microns in one pass. As a result of rolling 3 states with a total reduction of 30, 50 and 70% were obtained. Deformed specimens were annealed at 850°C after rolling and then quenched in water.

Structural studies of titanium β-alloys were carried out using optical microscope Olympus 71 and scanning electron microscope Quanta 600 FEG with a field emission gun. Investigation of the structural-phase composition and the crystallographic texture was also performed using the methods of automatic analysis of the electron back-scattered diffraction patterns (EBSD) on scanning electron microscope Quanta 600 FEG at an accelerating voltage of 20 kV, beam currents of 13 nA, and software TexSEM Lab (TSL). X-ray studies performed on a universal X-ray diffractometer, ARL X' tra.

Specimens for the above methods were cut using electrical discharge machine, and then subjected to mechanical grinding to install TegraPol-31 firm "Struers". Preparation of the sample surface for optical metallography and X-ray diffraction (XRD) analysis included chemical etching in a solution of 4 ml HF, 6 ml HNO₃ and 190 ml H₂O, for scanning electron microscopy using electrolytic polishing at the facility LectroPol-5 (Struers) in a solution of 60 ml of HClO₄, 600 ml CH₂OH and 360 ml CH₃(CH₂)CH₂OH at voltage U = 50 V.

Mechanical tensile tests were carried out on a universal floor electromechanical testing machine Instron 5882 with a strain rate of 1.5 mm / min. The test samples were cut at electrosparkering machine in the form of double blades with working part 2.88 x4,08x38 mm³. Further, the surface of samples subjected to mechanical grinding. According to the results of tests the elastic modulus, yield strength and tensile strength, ductility were evaluated. Modulus of elasticity was evaluated from the slope of the elastic part of stress-strain curve.

3. Results and discussion
The microstructure of the cold-rolled samples of the alloy Ti-26Nb-7Mo-12Zr with a total deformation of 30 and 60% after annealing is represented by partly recrystallized grains, the volume fraction of which is 43 and 94, respectively (figure 1a, b). According to the analysis of electrons back-scattered diffraction patterns (figure 2) the formation and growth of recrystallization nuclei occurs at high-angle boundaries of the original deformed grains. As a result of cold rolling and subsequent annealing with quenching the average size of grains of the alloy decreased by an order of magnitude in compare with the initial state and makes 20,5 ± 0,9 μm (30% deformation and annealing followed by quenching) and 10,1 ± 0,3 μm (60% deformation and annealing followed by quenching).

In the alloy Ti-26Nb-7Mo-12Zr after rolling with a maximum degree of deformation (90%) in contrast to the previous state (with a lesser deformation degree), recrystallization was complete. It led to the formation of a homogeneous globular structure (figure 1c, 3). As can be seen from the presented in Figure 3 histogram of grain size defined by a secant average grain size is 9 μm. As it can be seen from images of the microstructure, there are observed areas with large and small grains. 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 EBSD patterns it was found that in the studied alloy with fully recrystallized structure most of the boundaries represent the high-angle grain boundaries. The volume fraction of such grains is ~ 80% (figure 3a).
Figure 1: The image of the microstructure of the alloy Ti-26Nb-7Mo-12Zr after rolling at room temperature with the degree of deformation a) 30% b) 60%, c) 90% and subsequent annealing at $T = 850^\circ$C followed by quenching (scanning electron microscopy).

Figure 2: Map of the distribution of crystallographic orientations and map of grain boundaries misorientations (green - low-angle, blue - high-angle grain boundaries) for alloy Ti-26Nb-7Mo-12Zr after rolling with a deformation degree 30% and subsequent annealing followed by quenching.

Measurement of the elastic modulus showed that its value in the initial state is 84 GPa. As a result of cold rolling and subsequent annealing is a reduction of the elastic modulus. With increasing degree of preliminary cold deformation this value decreases (table 1). As can be seen from the data in the
table, strength characteristics following thermomechanical treatment changed slightly. In particular the plasticity increased in 1.5 times compared with the initial state.

Figure 3: Map of the distribution of crystallographic orientations (high-angle grain boundaries are marked) and histogram of the distribution of grains size for alloy Ti-26Nb-7Mo-12Zr after rolling with a deformation degree 90% and subsequent annealing followed by quenching.

Table 1. The mechanical properties of the alloy Ti-26Nb-7Mo-12Zr after preliminary cold deformation and annealing followed by quenching at T = 850°C.

| Preliminary cold deformation | Elastic Modulus, GPa | Yield strength, MPa | Ultimate strength, MPa | Flexibility, % |
|-----------------------------|---------------------|--------------------|------------------------|----------------|
| -                           | 83,7                | 793                | 800                    | 6,3            |
| 30%                         | 70,5                | 755                | 757                    | 5,5            |
| 60%                         | 69,2                | 767                | 768                    | 7,1            |
| 90%                         | 66,6                | 754                | 759                    | 8,5            |

4. Conclusion
The formation of a homogeneous globular structure of titanium β-alloys Ti-26Nb-7Mo-12Zr leads to a significant decrease in the modulus compared to the coarse-grained (initial) state and noticeable increase of plasticity without significant changing of the mechanical properties.

Acknowledgment
The work was carried out under a state contract "Biomedical research structural changes of organs and tissues during stent implantation of new generation" № 14.740.11.0182.

References
[1] Kolobov Yu R 2009 Nanotechnologies in Russia 11-12 758
[2] Leyens C and Peter M 2003 Titanium and Titanium Alloys. Fundamentals and Applications (Weinheim)
[3] Hanawa T, Hiromoto S and Yamamoto A 2001 Structural biomaterials for the 21 century 145
[4] Geetha M, Singh A K, Asokamani R and Gogia A K 2009 Progress in materials science 54 397
[5] Yoshimitsu Okazaki, Sethumadhvan Rao, Yoshimasa Ito and Tetsuya Tateishi 1998 Biomaterials 19 1197
[6] Nakai M, Niinomi M and Akahori T 2008 Advances in Materials Research 10 167
[7] Hench L and Jones D 2007 Biomaterials, artificial organs and tissue engineering (Moscow: Technosphere)
[8] Niinomi M, Kuroda D and Fukunaga K 1999 Titanium 99: Science and technology ed Froes F H and Caplan I (The Minerals, Metals&Materials Society) pp 1195-11201
[9] Kawahara H 1992 Bulletin of the Japan Institute of Metals 31 1033-1039