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MECHANICAL PROPERTIES OF NANOSTRUCTURED TITANIUM WITH BIOACTIVE TITANIUM-ORGANIC NANOCOATING

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Abstract. We present here the results of the study of mechanical properties of the nanostructured titanium samples fabricated by means of the severe plastic deformation that has titanium organic brush-like nanostructures on the surface. Based on the mechanical properties of the samples, we established for the first time that the gas-phase ALD synthesis at 200-400 °C of titanium organic nanocoatings with height of 220 nm and the distances between nanostructures up to 200 nm does not lead to deterioration of the mechanical properties of the nanostructured titanium.

Keywords: nanostructured titanium; equal channel angular pressing; brush-like nanostructure; titanium organic nanocoating; mechanical properties.

1. Introduction

The traditional metallic biomaterials reached the limit of the durability. These materials must correspond to the definitive requirements to be used as the medical pieces. They must be bioactive and biocompatible and also the materials should have high mechanical durability, especially under the cyclic loads that is important for the long-term usage of the produced medical pieces.

Currently, titanium and its alloys are known as the most successful materials for the fabrication of orthopedic and dental implants [1].

Currently, nanostructured metallic titanium (nanotitanium) is intensively studied [2, 3]. This material has better mechanical properties as compared with the pure titanium.

Particularly, severe plastic deformation of titanium and its alloys by means of equal channel angular pressing (ECAP) is used for the fabrication of nanotitanium with ultimate tensile strength higher than 1000 MPa [2, 4]. Due to the sufficiently high mechanical durability of pure titanium, we can avoid the addition of toxic additives. Titanium and nanotitanium are not toxic. However, additional surface modification is required for improvement of the biomedical properties of the titanium implant.

There are the several approaches for the improvement of survival rate of metal implant that are based on the application of the specific bioactive and biocompatible coatings [5-10]. However, chemical action of the reagents on the material surface at 200-400 °C can lead to the change of the mechanical properties of nanotitanium. Despite the fact that to date the mechanical properties of nanotitanium are studied in detail, there is no information about the influence of the chemically fabricated coatings (e.g. by Atomic Layer Deposition – ALD [11]) at high temperatures on the mechanical properties and the structure of nanotitanium.

The goal of this work was to study the influence of the brush-like titanium-organic nanocoatings on the titanium on the mechanical properties of the nanotitanium samples.

2. Experimental

The most important characteristics of the bulk material (metal) are its microstructure and mechanical properties. Given the above, certification of the microstructure of experimental samples was performed. The average size of nanotitanium grains was determined; mechanical tensile tests and fatigue tests were conducted.

To determine the effect of nanostructured brush-like coatings on the set of mechanical characteristics of experimental samples of nanotitanium, we prepared the samples with coatings and without coatings. Nanotitanium samples were prepared at the same conditions from the long ingot of the nanostructured Grade 4 titanium obtained by ECAP-Conform prrocessing with subsequent drawing [2, 3].

Table 1. Structural characteristics of the nanotitanium samples with brush-like titanium-organic nanocoatings (samples 1-3) according to AFM and SEM.

Name	Sample			
Synthesis conditions	nanotitanium	1	2	3
Temperature of the nanotitanium surface	-	300	400	400
Synthesis temperature, °C	-	200	200	200
Number of the treatment cycles, n	-	20	15	20
Nanostructures size (width along X axis), nm	-	50-100	50-100	50-100
Nanostructures height (Rz), nm	-	7-36	15-35	50-220
Distance between nanostructures (S), nm	-	50-100	50-100	75-200

On the surfaces of the nanotitanium prepared for mechanical tests for stretching and fatigue strength, we synthesized brush-like titanium-organic nanocoatings [12].

The coatings were synthesized according to the conditions listed in the Table 1.

The nanostructures were coated using ALD - method [13-15].

According to Atomic Force microscopy (AFM) the surface of initial titanium support after such treatment is characterized by low roughness – average cluster height is ~1 nm.

The coatings were synthesized using the gas phase setup that provided the ALD reactions in the Ar gas stream.

Titanium tetrachloride ($TiCl_4$) and propargyl alcohol ($HC{\equiv}C\text{-}CH_2\text{-}OH$) were used as the reagents. Their vapors were transferred into the reactor by the argon stream at 200 °C. Before the synthesis, the nanotitanium plates were preheated in argon at 300 or 400 °C.

To be sure, in the repeatability of the results, five samples of each series were tested.

3. Results and discussion

The microstructure of nanotitanium samples without coating was analyzed by TEM (microscope JEOL JEM 2100) (Fig. 1).

We found that the structure is the mixture of the nanometer-sized grains. There are small grains of the size of 60-80 nm with the definitive boundaries with low dislocations density inside. Larger grains and fragments, 100-120 nm in size, contain high amount of dislocations. Average grains/subgrains size in nanotitanium samples was 100 nm.

All the mechanical tests were repeated for 5 samples of each series. The samples for the stretch tests (with diameter of 3 mm) were prepared according to the GOST 1497-84.

Strength characteristics of nanotitanium were tested using the universal testing machine Instron 5882 at room temperature with the speed of the crosshead of 1 mm/min. The fatigue life of the nanotitanium was tested using the universal testing machine Instron 8801.

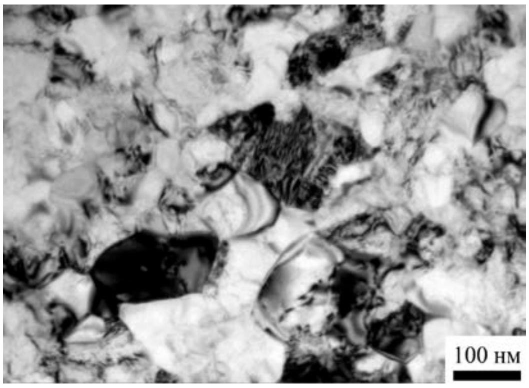


Fig. 1. Nanotitanium microstructure.

3.1. Mechanical properties of the nanostructured titanium. In order to determine mechanical properties of nanotitanium, the tensile tests of cylindrical specimens have been carried out. The results of these tests are given in the Table 2, whereas the results of fatigue tests – in the Table 3.

Table 2. Mechanical properties of the nanostructured titanium samples.

Sample	Temperature T, °C	Conditional yield strength $\sigma_{0,2}$, MPa	Tensile strength $\sigma_в$, MPa	Relative elongation, δ, %
nanotitanium	20	1237	1290	10.9

Table 3. Fatigue life of the nano titanium experimental samples.

Sample	Temperature T, °C	Number of cycles	Endurance limit σ_{-1}, MPa	Note
nanotitanium	20	1×10^6	590	Not destroyed

At the initial stage of mechanical testing, extensive hardening of nanotitanium has been observed, that is related to increased dislocations density in the material. Further, when the deformation degree increases, after reaching of the maximum current, stress decrease is observed associated with the formation of neck in the region of strain localization.

According to the data given in the Table 3, nanotitanium samples without coatings withstood $1 \cdot 10^6$ loading cycles at the load of 590 MPa without destroying.

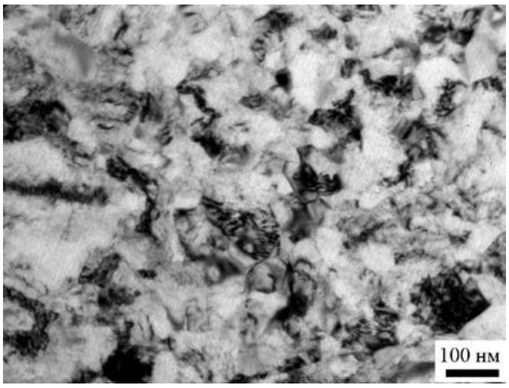
Total load error during the test did not exceed ±3 % at f = 50 Hz.

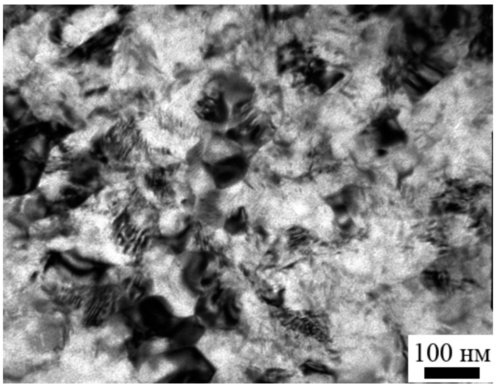
In general, for the studied nanotitanium samples without coating the average values of the ultimate strength, conventional yield strength and elongation were equal to: $\sigma_в$ = 1290 MPa, $\sigma_{0,2}$ = 1237 MPa and δ = 10,9 %, endurance limit after 10^6 cycles is σ_{-1} = 590 MPa.

3.2. Mechanical properties of nanotitanium with brush-like titanium organic coatings on the surface. TEM analysis of the microstructure of nanotitanium with brush-like titanium organic coatings is presented on Fig. 2.

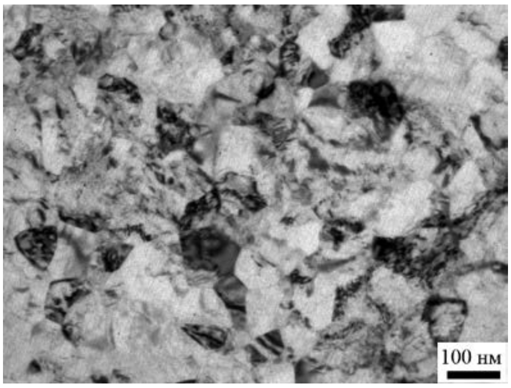
Evidently, synthesis of coatings and thermal treatment of nanotitanium samples while coating, does not lead to a change in the size of grains and subgrains in the titanium structure. Average grains and subgrains size was 100 nm. However, boundaries for the most crystallites become more explicit and the dislocations density inside of the structure elements decreases. Such changes of the internal grains structure is called the return of the first kind [15]. It is characterized by the redistribution of the crystal lattice defects without formation and migration of the sub-boundaries.

To study the influence of coatings on mechanical properties of nanotitanium, we conducted mechanical tests of cylindrical samples of coated nanotitanium (Table 4). Five samples were tested for each series in order to be sure in the repeatability of the results.





Sample 1 Sample 2



Sample 3

Fig. 2. Microstructure of nanotitanium samples with brush-like titanium organic coatings on the surface.

Evidently, the maximum current stress value in coated nanotitanium samples slightly decreased (in average, by 24 MPa), whereas relative elongation is increased.

Table 4. Mechanical properties of nanotitanium with brush-like titanium organic coatings on the surface.

Sample	Temperature T, °C	Conditional yield strength $\sigma_{0,2}$, MPa	Tensile strength σ_B, MPa	Relative elongation δ, %
HMT	20	1237	1290	10.9
1	20	1175	1266	11,1
2	20	1173	1255	11,5
3	20	1171	1253	11,6

Comparing to the non-coated nanotitanium, the mechanical behavior of titanium with brush-like coatings was rather similar. In all the samples, we observe hardening at the initial deformation stage, reaching of maximal yield strength with subsequent softening and destroying of the sample.

All the experimental samples survived after $1 \cdot 10^6$ loading cycles (Table 5) at load of 590 MPa without destroying.

Table 5. Fatigue life of nano titanium samples with the brush-like titanium organic surface coatings.

Sample	Temperature T, °C	Cycles number, N	Endurance limit σ_{-1}, MPa	Note
1	20	1×10^6	590	Not destroyed
2	20	1×10^6	590	Not destroyed
3	20	1×10^6	590	Not destroyed

4. Conclusions

In the present work, it was shown that the application of organic titanium nano-coating on the surface of nanostructured titanium in gas-phase in the temperature range 200-400 °C does not lead to deterioration of the mechanical properties of nanostructured titanium.

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