Physicomechanical properties of Ti-Ta-based surface alloys synthesized on the NiTi shape memory alloy

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Abstract. This paper presents a research data on investigation of physicomechanical properties of Ti-Ta-based surface alloys, synthesized on the NiTi-substrate. The Ti-Ta-based surface alloys were formed in a single vacuum cycle, that comprises preliminary low-energy high-current pulsed electron beam (LEHCPEB), Ti-Ta film deposition by magnetron sputtering, and pulsed electron beam melting of the system “Ti-Ta-based surface alloy/NiTi-substrate”. Experimental investigation and analysis of physicomechanical properties of Ti-Ta-based surface alloys on the NiTi-substrate were performed by method of nanoindentation. Our data suggest that the electron beam synthesis of Ti-Ta-based surface alloys, different in thickness and composition on the NiTi-substrate, leads to a gradient change of physicomechanical parameters. Modification of the surface of NiTi alloy changed the functional (pseudoelastic) properties by no more than 10%.

1. Introduction

Nowadays in the field of physics of hardening the surface of metallic materials different ways of combined processing are being developed. It can be electron beam and ion-plasma technologies [1]. The surface treatment of miniature devices (actuators), that are applicable in the field of microelectronics [2], by magnetron sputtering of alloying components and subsequent pulsed melting by a low-energy high-current pulsed electron beam (LEHCPEB) makes it possible to form thin layers on the surface of miniature devices. They are termed surface alloys (SA) and provide high adhesion to metallic substrate [3].

However, it is known that modification of the surface of miniature devices based on nickel titanium alloy (NiTi) does not always have a positive influence on their integral physicomechanical properties. This is important to consider during the processing of the functional NiTi alloy, which has the unique shape memory effect (SME) and superelasticity (SE). Therefore, it is necessary to understand the impact of treatments on functional (pseudoelastic) SME-SE properties during the modification of physicomechanical characteristic of the surface of miniature devices.

At the moment, a precision method of investigation and analyzing physicomechanical properties is a nanoindentation. Especially, this method is useful to evaluate the physicomechanical characteristics of modified layers. Such testing can identify differences in elastic and plastic behavior of materials with thin films and coatings, including those with a multilayer gradient structure [4, 5].

The purpose of this work is to investigate physicomechanical properties of Ti-Ta-based surface alloys synthesized on the NiTi shape memory alloy.
2. Experimental

2.1. Material
The material investigated here is commercial NiTi alloy produced as rolled sheets by vacuum induction melting (MATEK-SMA, Russia). The chemical composition of the alloy was: Ti (balance); 55.08 Ni; 0.051 C; 0.03 O; 0.002 N (wt %). The substrate was spark cut to dimensions of 10x10x1 mm by electrical discharge machining (EDM), chemically cleaned, electrolytically polished and washed in an ultrasonic bath with distilled water.

2.2. Formation of Ti-Ta-based surface alloys
The Ti-Ta-based surface alloys were formed on modified automatic setup RITM-SP (Microsplav, Russia), described in detail in Ref. [3, 6]. To avoid crater formation and local separation of the Ti-Ta film during pulsed melting the NiTi-substrate was preliminary irradiated with LEHCPEB at a pulse duration $\tau = 2-2.5$ μs, beam energy density $E_s = 3.4 \pm 0.7$ J/cm$^2$, and number of pulses $n = 32$. Thereafter, the NiTi-substrate was positioned by a manipulator along the magnetron sputter axis for deposition of Ti-Ta film of ~ 50 nm thickness, and along the electron beam axis for pulsed melting of the film-substrate system at regime: $E_s = 2 \pm 0.2$ J/cm$^2$, and $n = 5$.

The Ti-Ta-based surface alloys were created on the basis of films of two compositions: Ti$_{70}$Ta$_{30}$ and Ti$_{60}$Ta$_{40}$ (at %). The number of deposition-melting cycles were $N = 20$ and 30, respectively, so that the melted films were in total no thicker than ~ 1 and ~ 1.5 μm. Further in the text, these modified surface layers denoted as Ti$_{70}$Ta$_{30}$-based SA, and Ti$_{60}$Ta$_{40}$-based SA.

2.3. Nanoindentation
Investigation of strength and elastoplastic parameters of Ti-Ta-based surface alloys on the NiTi-substrate were examined by nanoindentation on a Nano Hardness Tester (CSM, Switzerland). As a result of the experiment, a series $P$-$h$ diagrams (loading/unloading) were obtained. At a figure 1 $P$-$h$ diagram demonstrates the displacement of the indenter as function of applied load.

![Figure 1](image_url)

**Figure 1.** Example of a load-displacement curve for a single loading cycle of indentation ($h_{\text{plastic}}$ – residual depth after unloading; $h_{\text{pseudoelastic}}$ – pseudoelastic depth recovery; $h_{\text{elastic}}$ – elastic depth recovery; $h_{\text{max}}$ – maximum indentation depth).
According to the obtained $P$-$h$ diagrams, using the Oliver-Pharr method \[7\], the dynamic microhardness $H_{OP}$, and Young’s modulus $E$ were determined.

The plasticity characteristic $\delta_H$ of surface layer shows the propensity of the material to deform under the action of the load. This parameter was estimated using the methodology \[8\]:

$$\delta_H = 1 - 14,3 \left( 1 - \nu - 2 \nu^2 \right) \frac{HV}{E}$$  \hspace{1cm} (1)

where $\nu$ – Poisson’s ratio; $HV$ – Vickers microhardness; $E$ – Young’s modulus of examined material.

Pseudoelastic properties of surface layer were estimated using the parameter $\eta$. It characterizes the degree of pseudoelastic recovery of the indentation area \[9\]:

$$\eta = \frac{h_{\text{max}} - h_{\text{plastic}}}{h_{\text{max}}} \times 100$$  \hspace{1cm} (2)

where $h_{\text{max}}$ – maximum indentation depth; $h_{\text{plastic}}$ – residual depth after unloading (figure 1).

3. Experimental results and discussion

3.1. Physicomechanical properties of NiTi-substrate

The physicomechanical properties of surface layers of initial NiTi can be addressed from figure 2 showing Young’s modulus $E$ (1), dynamic microhardness $H_{OP}$ (2), and plasticity characteristic $\delta_H$ (3) as a function of maximum indentation depth $h_{\text{max}}$ under increasing load $P$ from 5 up to 300 mN.

![Figure 2. Dependences of $E$ (1), $H_{OP}$ (2), and $\delta_H$ (3) on the maximum indentation depth $h_{\text{max}}$ for initial NiTi-substrate.](image)

It is seen that near the surface of the initial sample the physicomechanical parameters are: $E \approx 55$ GPa, $H_{OP} \approx 3.5$ GPa, $\delta_H \approx 0.5$. Next, these parameters linearly change at a depth $h$ more than $\sim 1.5$ μm to the values: $E \approx 45$ GPa, $H_{OP} \approx 3$ GPa, $\delta_H \approx 0.45$. An increase of microhardness and Young’s modulus in the surface layers being indicative of surface hardening. This is due to the manufacturing of NiTi alloy that was fabricated as rolled sheets by vacuum induction melting.

3.2. Physicomechanical properties of the systems “Ti-Ta-based surface alloy/NiTi-substrate”

Figure 3a illustrates the physicomechanical properties of the Ti$_{70}$Ta$_{30}$-based SA ($\sim 1$ μm). It is seen that the modification of the NiTi alloy leads to gradient change of physicomechanical characteristics.
In the surface layer of ~700 nm thickness, the gradient of their variation is greater than in the sublayer, which is being located at a depth of more than ~1 μm (i.e. at a depth more than calculated thickness of the Ti_{70}Ta_{30}-based SA). Comparing the research data on investigation of the structure (TEM/EDS) [10] with the results of this work, it follows that the structure of the Ti_{70}Ta_{30}-based SA (~1 μm) provides a more significant effect on the physicomechanical properties than the sublayer structure, which is being located at a depth h from ~1 to ~2 μm. It was established [10] that this sublayer corresponds to a transition (diffusion) zone between the Ti-Ta-based surface alloy and NiTi-substrate. This means that the presence of an extended intermediate zone at a depth h from ~1 to ~2 μm provides a gradual change in the physicomechanical characteristics and high adhesion of the Ti-Ta-based surface alloy to the NiTi-substrate. Further, according to [10], the layer of NiTi-substrate located a depth of ~2 to ~2.5 μm. In this layer the structure was modified during formation of SA by multiple pulsed heating in the pre-melting mode (without actual melting).

![Figure 3](image_url)

**Figure 3.** Dependences of $E$ (1), $H_{OP}$ (2), and $\delta_{Hi}$ (3) on the maximum indentation depth $h_{max}$ for Ti_{70}Ta_{30}-based SA/NiTi-substrate (a), and Ti_{60}Ta_{40}-based SA/NiTi-substrate (b).

Figure 3b demonstrates the physicomechanical properties of the Ti_{60}Ta_{40}-based SA (~1.5 μm). It is seen that gradient change in the properties is more gradual and continuous (more than ~1 μm), unlike Ti_{70}Ta_{30}-based SA (figure 3a). When the depth of the calculated thickness of Ti_{60}Ta_{40}-based SA is reached, the physicomechanical properties in the sublayer (at depth ~1.5 to 2.5 μm) stabilize and do not change their values. This character of change of the physicomechanical parameters of the Ti_{60}Ta_{40}-based SA is obviously due to the peculiarity of the influence of modification to the structure, which requires independent investigations.

A comparison of the physicomechanical characteristics of surface alloys, different in thickness and composition, showed (figure 3a, b) that near the surface (at a depth of up to ~500 nm) the physicomechanical parameters differ: $E \approx (95\pm5)$ GPa, $H_{OP} \approx (7\pm1)$ GPa, and $\delta_{Hi} \approx 0.5$ for Ti_{70}Ta_{30}-based SA; $E \approx (75\pm15)$ GPa, $H_{OP} \approx (6\pm1)$ GPa, and $\delta_{Hi} \approx 0.45$ for Ti_{60}Ta_{40}-based SA. These parameters become close to each other in magnitude at a depth of more ~1.5 μm.

### 3.3. Functional (pseudoeelastic) properties of the systems “Ti-Ta-based surface alloy/NiTi-substrate”

As is known [11], modification of the surface of nickel titanium alloy, including the pulsed electron beam action, leads to hardening of the surface layers of the material. This causes the suppression of the important functional properties of the alloy, such as SME-SE. An efficient way to investigate functional properties in surface modified layers is to use the method of estimating the degree of pseudoeelastic shape recovery $\eta$ of the indentation area, which confirmed itself in [4, 9].
Figure 4 shows the results of the dependence of shape recovery ratio $\eta$ on the maximum indentation depth $h_{\text{max}}$ for initial NiTi-substrate (figure 4, curve 1), and for NiTi samples after formation of Ti-Ta-based surface alloys (figure 4, curve 2, 3).

The parameter $\eta$ varies within the layer of $\sim 2 \mu m$ thickness in both Ti-Ta-based surface alloys. That is the presence of Ti-Ta-based surface alloys changed the functional (pseudoelastic) properties in modified layers (at depth of up to $\sim 1 \mu m$) by no more than $\sim 10\%$. In the underlying sublayers (at depth of more $\sim 1 \mu m$), shape recovery ratio $\eta$ remains constant and less than in the surface layer by no more than $\sim 5\%$.

4. Conclusion
The main conclusions obtained in the work:

1. Electron beam synthesis of Ti-Ta-based surface alloys, different in thickness and composition on the NiTi alloy, leads to a gradient change of physicomechanical parameters.

2. The strength and elastic-plastic parameters of Ti-Ta-based surface alloys are different from each other, but become close in magnitude at a depth of more than $\sim 1.5 \mu m$.

3. Modification of the surface of NiTi alloy changed the functional (pseudoelastic) properties by no more than $\sim 10\%$.

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