Formation of Ti-Ta-based surface alloy on TiNi SMA substrate from thin films by pulsed electron-beam melting

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Abstract. TiNi shape memory alloys (SMAs) are unique metallic biomaterials due to combination of superelastisity and high corrosion resistance. Important factors limiting biomedical applications of TiNi SMAs are a danger of toxic Ni release into the adjacent tissues, as well as insufficient level of X-ray visibility. In this paper, the method for fabrication of protective Ni-free surface alloy of thickness ~1 μm of near Ti70Ta30 composition on TiNi SMA substrate has been successfully realized. The method is based on multiple alternation of magnetron co-deposition of Ti70Ta30 thin (50 nm) films and their liquid-phase mixing with the TiNi substrate by microsecond low-energy, high current electron beam (≤15 keV, ~2 J/cm²) using setup RITM-SP (Microplav, Russia). It was found by AES, XRD, SEM/EDS and HRTEM/EDS examinations, that Ti-Ta surface alloy has an increased X-ray visibility and gradient multiphase amorphous-nanocrystalline structure containing nanopores.

1. Introduction
Successful biomedical applications of TiNi alloys exhibiting shape memory effect and superelasticity (SME-SE) are associated with their ability to reversible return a substantial predetermined strain (8–12%) when heated to body temperature [1, 2]. Important factors limiting these applications, particularly, in cardiovascular surgery, are a danger of release of toxic Ni into the adjacent tissues [3,4], as well as their insufficient level of X-ray visibility [5].

The optimum solution of these problems seems to produce a protective surface layer up to several micrometers in thickness which would possess not only excellent biochemical resistance, but also high biomechanical properties under cyclic loading in aggressive biological media. This approach can be realized by producing a surface alloy which would have mechanical properties (elastic modulus and SME-SE characteristics) similar to these of TiNi substrate, but free of nickel. Surface alloys, as known, are produced by pulsed melting of an alloying film with a substrate and/or by ion implantation [6]. That is why, surface alloys, compared to conventional PVD and CVD-based coatings, do not present problems associated with poor adhesion and delamination. In this respect, the Ti-Ta system, whose alloys possess high-temperature SME (HTSME), looks very promising. The martensitic transformation (MT) temperature range of these alloys is 50–100 °C above ambient temperature [7], so, they are in martensitic states with elastic characteristics comparable to these of muscle tissues at
human body temperature. In addition, alloying of titanium alloys, including TiNi SMAs, with tantalum improves their corrosion resistance [8], biocompatibility [9], and X-ray visibility [10].

This work aims to fabricate and characterize the novel thin (1–2 μm) protective surface layers based on Ni-free alloys with superelastic properties on TiNi substrates. The paper presents the results of studies of elemental and phase compositions as well as structure of ~1-μm-thick Ti-Ta thin-film coating and Ti-Ta-based surface alloy fabricated on TiNi substrate by magnetron co-deposition of Ti-Ta films followed by pulsed melting by microsecond low-energy, high-current electron beam (LEHCEB) [11].

2. Experimental

Fabrication of Ti-Ta-based surface alloy was performed in united vacuum cycle using modified automatic setup RITM-SP equipped with LEHCEB source, DC-magnetron sputtering unit and common vacuum chamber evacuated by turbomolecular pump [12]. Magnetron unit consisted of three magnetrons arranged symmetrically on a circle, two of which contained Ti (VT1-0, Russia) and Ta (GIRMET, Russia) targets of 75 mm diameter. The angle between magnetron axis and the normal to substrate holder was 28°. The co-deposition of Ti70Ta30 (at.%) thin films was carried out at room temperature at Ar working gas of 0.1 Pa in a vacuum chamber with a base pressure of ~10−3 Pa. 560 and 160 W power were applied to Ti and Ta targets, respectively, which corresponded to the film codeposition rate of 1.8 ± 0.3 nm/s. The substrate was rotated with the rate of 20 rpm during the co-deposition to obtain a homogeneous film composition over the substrate.

Substrates with the dimensions of 15×10×1 mm were made of commercial (VIM) TiNi alloy (MATEK-SMA Ltd., Russia). Its chemical composition was as follows (wt%): 55.08 Ti, 0.051 Ni, 0.03 C, 0.002 O; and the transformation temperature A1 = 303 K. The methods for preparing TiNi substrates as well as their microstructural characterization are given in [13]. To prevent the local delamination of a Ti-Ta film due to cratering during the pulsed melting [13], the substrate was pre-irradiated with LEHCEB in the following mode: pulse duration of 2–2.5 μs, maximum electron energy of 25 keV, energy density of 3.8±0.7 J/cm²; beam diameter of ~60 mm, number of pulses n = 32, and repetition rate of 1 pulse/5 s. After this pre-treatment, TiNi substrate was installed by manipulator alternately along the magnetron unit axis for co-deposition of 50-nm-thick Ti70Ta30 film, and along the LEHCEB axis for pulsed melting of film/substrate system. Pulsed melting was performed in the following mode: maximum electron energy of 15 keV, of 2±0.2 J/cm²; n = 5.

The thickness of Ti70Ta30 film, energy density and number of pulses in each cycle of "co-deposition + pulsed melting" were chosen based on the two main requirements: (i) a thickness of the melted layer of a film/substrate system should be a little more than ~1 μm; (ii) a liquid-phase diffusion depth of film components into substrate must be, at least, several times greater than original film thickness to provide a diffused transition between Ti-Ta surface alloy and TiNi substrate. The number of cycles of "co-deposition + pulsed melting" was N = 20; thus, the predicted thickness of Ti70Ta30 surface alloy was ~1 μm. The energy density of LEHCEB was preliminarily controlled by calorimeter with an accuracy no worse than ±15%.

Elemental depth profile analysis of test samples was performed by Auger electron spectroscopy (AES) (Shkhuna-2, Russia) at sputtering rate of analyzed near-surface layer of 2÷3 nm/min and 3 keV Ar+ ion beam diameter of 1 mm; maximal analyzed depth is 400 nm. The average elemental compositions of Ti-Ta coating and surface alloy were determined with the INCA Energy Dispersive Spectrometer (EDS) (Oxford Instruments, UK) installed on scanning [EVO 50 (Zeiss, Germany)] and transmission (JEM 2100; the electron-probe diameter was ~12 nm) electron microscopes (SEM, TEM). X-Ray diffraction (XRD) analysis was carried out on DRON-7 diffractometer (Burevestnik, Russia) with Co-Kα radiation in symmetric and asymmetric Bragg diffraction geometry. XRD patterns in asymmetric geometry were obtained at glancing incidence angles α = 3, 5, 8 and 15°. TEM experiments were performed on JEM 2100 electron microscope (JEOL, Japan) at accelerating voltage of 200 kV by the method of thin foils. Thin foils were made by ion thinning using EM 09100IS device.
(JEOL, Japan) from thin (0.3 mm) plates, spark-cut perpendicularly to the plane of the samples. This enabled studying the microstructure at different depths below the surface.

3. Results and discussion

3.1. Elemental composition

3.1.1. Ti-Ta thin-film coating. According to AES data, as-co-deposited ~1-μm-thick Ti-Ta coating was oxygen-enriched up to a depth of ~50 nm. This is because the Ti/Ta films absorb residual oxygen from vacuum chamber. The coating was uniform in composition at the depths x ≥ 50 nm, and their composition was Ti_{80}Ta_{20} (at.%) at x = 200 nm. Similar measurements were performed by SEM/EDS analysis to clarify the coating composition. Figures 1a, 1b and 1c shown the results of SEM/EDS surface analysis of the coating at accelerating voltage of 10 kV, wherein, taking into account the density of Ti-Ta coating/ alloy, the thickness of the analyzed surface layer is ~0.5 μm [14]. According to data obtained by averaging over 6 EDS measurements, the coating composition is Ti_{70}Ta_{30} (at.%) in accordance with the prediction. The content of O and C impurities in the coating is less than the limit of detection (LOD), i.e. ≤4-5 at.%. 

3.1.2. Ti-Ta-based surface alloy. According to AES data, the ~50 nm-thick near-surface layer of Ti-Ta surface alloy, as that of Ti-Ta coating, is enriched by oxygen, which delivered into the melt from residual atmosphere of vacuum chamber during processing. The surface alloy is homogeneous in composition at depths x ≈ 50÷350 nm, but, in contrast to the coating, it contains nickel, and its composition is Ti_{40}Ta_{30}Ni_{11}O_{5}C_{5} (at.%) at intermediate depth of 200 nm. In turn, SEM/EDS analysis has shown (Figure 1e,f,g) that surface alloy, as co-deposited coating, has an average composition of Ti_{70}Ta_{30} (at.%) over thickness of ~0.5 μm. The presence of nickel (according to AES data) may be caused by its lower melting point, as compared to Ti and Ta, so it may segregate towards the surface from the molten substrate at the solidification front during multiple cycles of pulsed melting/solidification.

Figure 1. Results of SEM/EDS surface analysis for Ti-Ta coating (a-d) and Ti-Ta based surface alloy (e-h): EDS map distributions of Ti (a, e) and Ta (b, f); SEM images (c, g); EDS spectrums (10 keV) (d, h) obtained by averaging over 6 points shown in (c) and (g), correspondently.

3.2. Phase composition

Figure 2 shows XRD patterns of TiNi substrate in the initial state, the substrate with co-deposited Ti-Ta coating and the substrate with Ti-Ta surface alloy. Analysis of XRD patterns given in Figure 2b, showed that Ti-Ta coating has multiphase structure composed of a bcc-phase based on β-Ti [15], β-
(Ti,Ta) [16], and α-Ta [17]. It follows from an analysis of the location of additional reflexes, that the coating can contain also one-component phases based on deposited Ti and Ta in their low-symmetric modifications: α-Ti with hexagonal structure [18] and β-Ta with tetragonal structure [19]. Significant broadening of main XRD reflexes indicates that the coating has nanocrystalline (domain) structure. The Ti-Ta-based surface alloy, as it follows from Figure 2c, has also multiphase structure, in which the main phase, most likely, is based on disordered Ti-Ta solid solution with amorphous-nanocrystalline structure.

Figure 2. XRD patterns of TiNi substrate (a), Ti-Ta coating (b) and Ti-Ta surface alloy (c, d), obtained in symmetric (a, b, c) and asymmetric (d) Bragg diffraction geometries; (d) glancing incidence angle α=15°. DSRs are located above the tangential (dotted) lines (d) in angular ranges of 40°-60° and 75°-90°.

The large number of clearly identified, although low-intensity reflexes is evidenced by the presence of martensitic α′- and α″- phases with composition close to Ti$_{70}$Ta$_{30}$ (at.%.) [16], as well as β-Ta-phase [19] in the surface layers. In turn, the broadening of corresponding reflexes point to the nanocrystalline (domain) structure of these phases.

XRD patterns, corresponding to the coating and to the surface alloy (Figures 2b and 2c), contain diffuse scattering regions (DSRs) in angular ranges of 40°-60° (Figure 2b,c,d) and 75°-90° (Figures 2c and 2d), indicating the presence of relatively large volume fraction (~5 vol.%) of quasi-amorphous phases. Angular positions of gravity centers of DSRs correspond to those of main XRD reflexes of bcc
phases based on pure Ti and Ta as well as on Ti-Ta system. This means that the short-range order in the atom arrangement in the quasi-amorphous and bcc phases is identical. From this, it follows that crystallization from the amorphous state will probably occur by the growth of bcc phases.

The XRD reflections from the B2 phase of TiNi substrate either absent (Figure 2b) or have very low intensity (Figure 2c). Taking into account symmetric Bragg diffraction geometry, this means that both Ti-Ta coating, and Ti-Ta surface alloy of thickness ~1μm absorb X-rays efficiently, and this is a reliable indication of their increased X-Ray visibility as compared with TiNi substrate.

The cross-section TEM examination of Ta-Ti-based surface alloy (Figure 3a) showed that its thickness is ~1 μm, which agrees with the expected value. Near the interface of surface alloy/substrate, an equiaxed polycrystalline structure with a average grain size of ~50 nm is formed. Surface alloy has slightly pronounced columnar structure, indicating on directional solidification in the process of formation. There are numerous nanosized inclusions having essentially spherical shape and different contrast (from white to dark gray). Inclusions are distributed non-uniformly in depth: increased inclusion density is observed near the interface of surface alloy/substrate.

Figure 3. Bright field TEM/HRTEM images of Ti-Ta-based surface alloy: (a) cross section view; (b) nanocrystalline particles embedded into the amorphous matrix; (c) nanopore inside the amorphous matrix.

The high-resolution TEM (HRTEM) analysis revealed a significant volume fraction of mixed amorphous-nanocrystalline structure in the surface alloy, signs of which were identified by XRD analysis. It is seen from Figure 3b, that individual nanocrystals with the size ≤10 nm are surrounded by regions with amorphous structure. The structure in a vicinity of typical white inclusion (presumably, nanopore) is shown in Figure 3c. One can see, that a conglomerate of nanocrystals with dark gray contrast is distributed along the boundary of white spherical precipitate, and, partly, inside it. This picture can be interpreted as a preferential nucleation and growth of nanocrystals on free surface (nanopore wall) in the matrix phase of the surface alloy. This result, which requires a separate study, can clarify the mechanisms of amorphization and crystallization of materials rapidly quenched from the melt.

According to TEM/EDS data, white inclusions contain oxygen (≥30 at.%) and argon (working gas). Chemical composition and shape of such inclusions (Figure 3a) indicate that they represent nanopores. Gray inclusions represent probably nanosized precipitates based on Ti, Ta, Ni (e.g., α’-Ti_{70}Ta_{30}, Ti_{2}Ni, Ta_{2}Ni). Different contrast of these particles is associated with their different chemical composition.

4. Conclusion
The method for fabrication of Ni-free surface alloy of thickness ~1 μm of near Ti_{70}Ta_{30} composition on TiNi SMA substrate has been successfully realized. The method is based on multiple alternation of magnetron co-deposition of Ti_{70}Ta_{30} thin films and their liquid-phase mixing with TiNi substrate by
microsecond LEHCEB. The Ti-Ta-based surface alloy has an increased X-Ray visibility and gradient multiphase amorphous-nanocrystalline structure containing nanopores. The immediate objectives are: (i) detailed studies of concentration depth profiles of the surface alloy; (ii) more detailed studies of the evolution of phase composition and atomic structure in depth by methods of grazing incidence X-Ray diffraction and HRTEM.

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