

# Surface Modification of TiNi Alloy by Electron Beam Influence<sup>1</sup>

L.L. Meisner, A.I. Lotkov, V.P. Rotshtein\*, A.B. Markov\*, V.V. Razdorskii\*\*, V.A. Kopsisova\*\*

*Institute of Strength Physics and Materials Science of SB RAS, pr. Akademicheskii, 2/1, Tomsk, 634021, Russia.  
Tel.:(3822)286989, Fax: +7(3822) 492-576, e-mail : llm@ispms.tsc.ru*

*\*Institute of High-Current Electronics of SB RAS, pr. Akademicheskii, 4, Tomsk, 634021, Russia.*

*\*\* Russian research and practice medicine center of SMI, Shestakova street,14, Novokusnetsk, 654034, Russia.*

**Abstract** – Results on elemental compositions and structural-phase conditions of the TiNi samples with a surface alloyed layers processed by the pulsed electron beam melting are reported. Before the treatment one part of the samples were covered by the layers (no more than 1  $\mu\text{m}$  in depth) of the alloying elements (Ti, Zr, Pd). An irradiation treatment was carried out by the low-energy ( $\sim 30$  keV) high current ( $\sim 30$  kA) electron beam (3–10 J/cm<sup>2</sup>, LEHCEB) pulsed with 2–3  $\mu\text{s}$  in time length. Chemical and structural conditions were studied by Auger electron spectroscopy and grazing incidence X-ray diffraction analysis. Nanohardness was measured by the CSEM Nano Hardness Tester. LEHCEBs influence of the uncovered TiNi-samples does not change the Ni, Ti and O concentration depth profiles. The influence by means LEHCEB of the covered TiNi-samples leads to the formation of a Ti–Zr–(Ni<20 at.%)–O and Ti–Pd–(Ni<20 at.%)–O surface layer at about 3–5  $\mu\text{m}$  in depth. Microhardness of the modified layer ( $\sim 300$  nm in depth) is fifth as higher as of the initial state. Samples with the surface-alloyed layers and/or the uncovered layers treated by LEHCEBs have a higher corrosion stability than the initial electropolished samples.

## 1. Introduction

Nowadays the titanium nickel alloys belong to the group of medical metal materials and are used for manufacturing of so-called the lifetime implants in dentistry, orthopaedy and cardiovascular surgery. During sterilization processing of the implant and/or its working within the human body there is a fast degradation of the TiO<sub>2</sub> thin oxide film and a dangerous of metal ions release (including the high toxic Ni ions) in adjacent human tissues or fluids [1]. An actual problem of physical and medical materials science is creation of barrier and bioinert layers or coatings on TiNi alloys surface with high corrosion stability in various active environments. Most of surface modification and coating technologies (chemical and thermo-chemical processing, plasma-oxide coatings, etc.) do not allow to solve this problem for the TiNi shape memory materials due to different obstacles: rather small thickness of an implanted and/or oxide layer, weak adhesion and delaminating

of the coated layers. In [2,3] we showed, that an extended homogeneity area of the B2-phase exists in system Ti-Ni-Zr – from 0 up to 20 at.% when Ti is substituted by Zr and from 0 up to 6 at.% when Ni is substituted by Zr. Thus, ternary Ti<sub>50-x</sub>Ni<sub>50</sub>Zr<sub>x</sub> alloys reveal a high-temperature shape memory effect (SME) and are characterized by high plasticity, accumulating 50–60 % of deformation before destruction, while Ti<sub>50</sub>Ni<sub>50-x</sub>Zr<sub>x</sub> are characterized by the wide temperature SME hysteresis. Additionally, It has been shown [4, 5], that corrosion stability is increased significantly in ternary TiNi-based alloys when the alloying elements are Zr, Pd, Pt, Au or when these elements are implanted in the subsurface layer. Unfortunately, it is impossible to use the ternary TiNiMe (Me: Zr, Pd, Pt, Au) alloys as medical SME or superelastic (SE) materials due to their high temperatures of SME (420 K and higher). Thus, the possibility of the controlled formation of the B2-single phase condition in the (sub-)surface layer alloyed by the elements, on the one hand, raising the corrosion resistance and, on the other hand, saving the martensitic transformation (MT) in the bulk is very important. The surface alloying of TiNi by the Zr, Pd, Pt, Au using the low energy high current electron beams (LEHCEBs) in the pulsed ( $\sim 10^{-7}$  s) melting regime [6–9] is a perspective way of increasing the materials corrosion resistance. However, regular investigations of the alloying processing using the LEHCEBs and its influence on corrosion properties of the TiNi alloys are very limited.

Investigation of the features and formation mechanisms of the element compositions, structural-phase conditions and thickness of subsurface composite layers, their mechanical properties (hardness, Young modulus) of the TiNi alloy depending on alloying elements and LEHCEBs parameters is aimed in the paper.

## 2. Materials and experimental methods

The studied Ti<sub>49.5</sub>Ni<sub>50.5</sub> alloy was prepared from nickel of grade NO and iodide titanium using sixfold arc remelting. MT and SME properties if this alloy

<sup>1</sup> This work is supported in part by the Siberian Branch of the Russian Academy of Science (project №91).

were investigated in details in [10, 11]. Samples with the size of  $(1 \times 15 \times 15) \text{ mm}^3$  for Auger electron spectroscopy (AES) and X-ray diffraction analysis (XRD) were used. Before the measurements, all samples were annealed at 1073 K for 1 h in vacuum higher than  $10^{-3} \text{ Pa}$  and then cooled in a furnace. Then the surface of the samples was etched electrolytically using a solution containing 90 % acetic acid and 10 %  $\text{HClO}_4$ . Then all samples were divided into the several groups. Before the LEHCEBs influence the thin films of the alloying elements (Ti, Zr, or Pd) were deposited with the special proportions on the samples surface. After that the LEHCEBs treatment was used with the following irradiation parameters: the energy density –  $(2 \div 10) \text{ J/cm}^2$ , the pulse duration –  $(2 \div 5) \mu\text{s}$  and numbers of pulses –  $(1 \div 10)$ .

The elemental composition of the samples was analyzed by Auger-spectrometer SHUNA-2 (AES analysis). The diameter of the probe electron beam was equaled to 1 mm, its energy was equal to 3 keV and the raster scan was  $10 \times 10 \mu\text{m}^2$  in size. The power resolution of the analyzer was 0.7 %. For surface cleaning and layer-by-layer sputtering, argon ion beam was used. The energy of argon ions was 3 keV; the beam diameter equaled 1 mm and the sputtering rate of the samples was equal to 2–3 nm/min. Phase composition in bulk of the alloys was studied by X-ray diffraction using a DRON-7.0 diffractometer. The phase compositions of the near surface layers were examined by grazing incidence X-ray diffraction analysis (GIXRD) using diffractometer XRD6000 (Shimadzu) with  $\text{Cu-K}\alpha$  radiation. By varying the incidence angle from 0.5 to  $10^\circ$ , depth dependent structural information from 0.15 to 10  $\mu\text{m}$  was obtained.

Investigation of the hardness, Young modulus and their depth dependences have been carried out on the LEHCEBs irradiated  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  samples without alloying films.

### 3. Results and discussion

The AES analysis of the Zr-alloyed layers of the  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  samples have shown that surface melting using pulsed the LEHCEBs results in the near-homogeneous distribution of Zr within the outer sub-surface layer in 2–2.5  $\mu\text{m}$  depth from the surface. Figure 1 illustrates an elements distribution within the alloyed layers formed after the same LEHCEBs impacts for two different thicknesses of the previously deposited films. It is seen, that at the equal LEHCEBs parameters more homogeneous layer is formed in the case of thinner films. While the average Zr-concentration in the layer is almost equal to 15 at.% for both cases. It is important to note, that Zr-alloyed layers are characterized by the Ni-depleted composition where Ni-contents has decreased almost twice in comparison with initial amount (50.5 at.%, Fig. 1). It is seen from Fig. 1 that the initial 49.5 at.%Ti-50.5 at.%Ni proportions of studied

alloy has not been achieved on depth more 3  $\mu\text{m}$  from the modified surface. Additionally, a pulsed melting of the "film-substrate" systems is not accompanied by the oxidation or carbonization the Zr-alloyed nor the Pd-alloyed layers. The fact is important for corrosion properties of TiNi-based alloys.

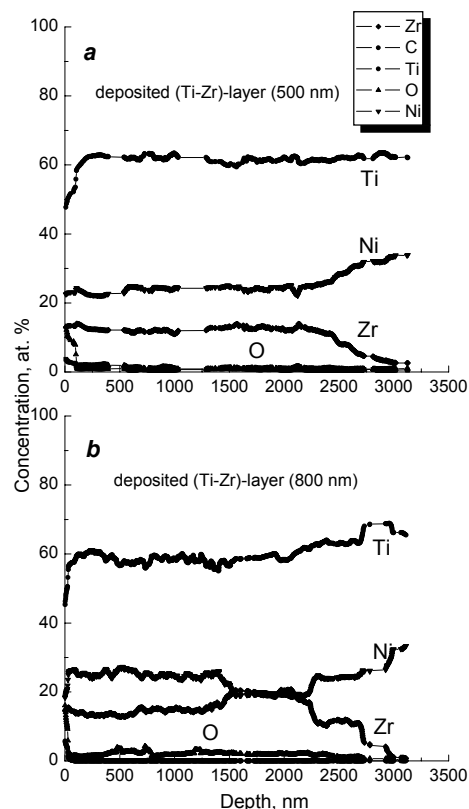


Fig. 1. An elements distribution within the Zr-alloyed layers of  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  samples after LEHCEBs impacts. Deposited films thicknesses are 500 nm (a) and 800 nm (b)

As seen from Fig. 1 and Fig. 2, the concentration uniformity of the Zr and Pd elements in the alloyed layers is reached at 10 pulses of LEHCEBs with the separate pulse duration about 2–3  $\mu\text{s}$ . Remarkably that significant concentration of Pd (10–15 at.%) is only achieved after an single LEHCEBs impact. The corresponding Pd-alloyed outer layer has thickness about 300 nm.

AES data have revealed that distribution both alloying and basic elements within the alloyed layers of  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  samples is homogeneous. Nevertheless the structural-phase compositions of the new subsurface layers were examined by XRD and grazing incidence X-ray diffraction analysis (GIXRD). By varying the incidence angle from 0.5 to  $10^\circ$ , depth dependent structural information from 0.15 to 10  $\mu\text{m}$  was obtained. It was found that the Zr-alloyed layer differs by their microstructure and phase compositions compare with the  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  substrate. Fig. 3 shows that intensity of the  $(110)_{\text{B}_2}$  X-ray Bragg peak decreases down to full disappearance at change of the X-ray grazing angle from 5

to  $2.5^\circ$ . At the same time, the broadening (diffuse) X-ray peaks of the pure Ti and Zr elements appear and their intensity grows with the  $\psi$ -angle decreasing. Hence, according to our preliminary GIXRD results the Zr-alloyed subsurface layer of  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  alloy generated with LEHCEBs by pulsed melting of "Zr-film –  $\text{Ti}_{49.5}\text{Ni}_{50.5}$ -substrate" system is nonhomogeneous in their structural-phase composition and microstructure. This layer has thickness about  $1\text{--}2\ \mu\text{m}$  and is characterized by absence of the initial B2-phase and segregation of the pure Ti- and Zr-films components. According to preliminary analysis of the peaks broadening the coherent-scattering region is about  $100\text{--}200\ \text{nm}$ . The gradual increase in the B2-phase volume fraction is observed in the underlying layer of  $2\text{--}5\ \mu\text{m}$  in depths (from a surface) with decreasing of the volume fraction of the Ti- and Zr-segregations. According to the XRD and GIXRD data the B2-lattice parameter in the modified layer is essentially less ( $a_{B2}=3.003\pm 0.002\ \text{\AA}$ ), than at an initial alloy ( $a_{B2}=3.0012\pm 0.002\ \text{\AA}$ ). It is necessary to note, that the B2-lattice parameter in subsurface areas of  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  samples are similar to its value ( $a_{B2}=3.0070\pm 0.0005\ \text{\AA}$ ) for samples of the same alloy modified by LEHCEBs without preliminary film coating [12].

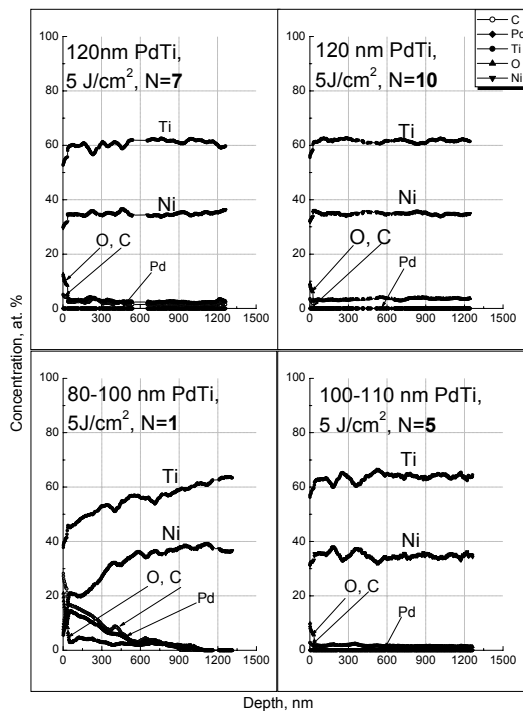


Fig. 2. An elements distribution within the Ti-Pd-alloyed layers of the  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  samples after LEHCEBs impacts with different pulse numbers  $N=1, 5, 7, 10$

The nanoindentation tests of the  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  samples modified by the LEHCEBs shows that this surface treatment leads to increase in hardness of the surface layer almost in 10 times thinner ( $100\pm 200\ \text{nm}$ ) in comparison with thickness of the layer with modified structural-phase condition. Figure 4 illustrates a depth penetration dependences of Vickers hardness and Young modulus

of modified and the nonmodified samples. As seen from Fig. 4 both hardness and elastic modulus of the outer surface layer of about  $100\ \text{nm}$  in thickness almost in 5 times exceed their values of initial nonmodified samples. One can add that the hardness of the nonmodified  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  samples obtained in this work is well coincide with the known data for titanium nickel [13].

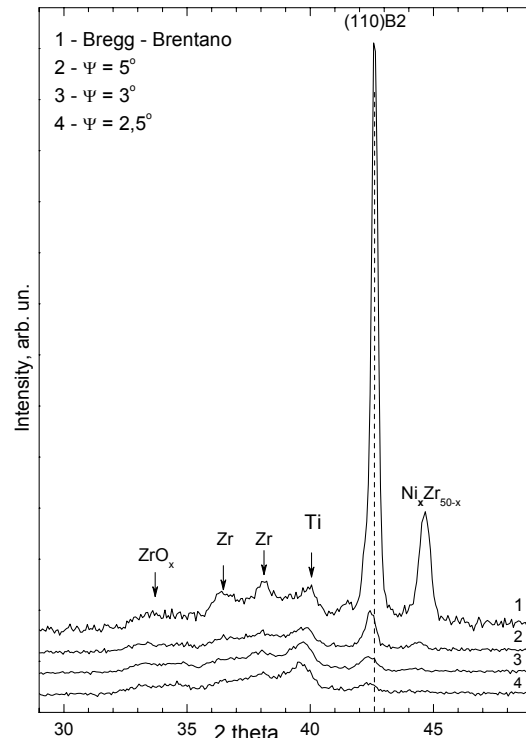


Fig. 3. XRD (1) and GIXRD (2–4) diffraction patterns of the  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  sample with Zr-alloyed surface layer modified by LEHCEBs

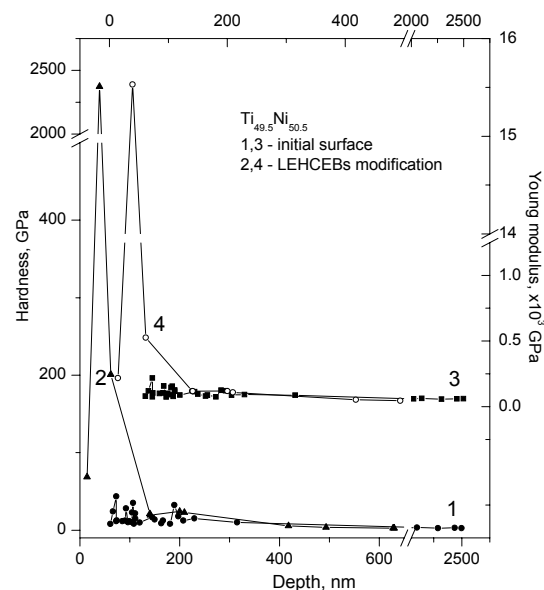


Fig. 4. The depth penetration dependences of Vickers hardness (1, 2) and Young modulus (3, 4) of the modified by LEHCEBs (2, 4) and the nonmodified (1, 3)  $\text{Ti}_{49.5}\text{Ni}_{50.5}$  samples

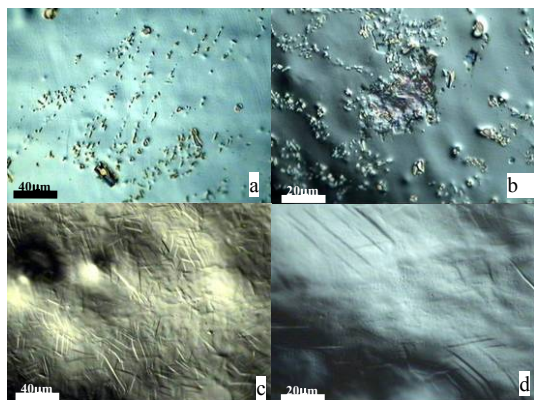


Fig. 5. Morphology evolution of nonmodified (a, b) and modified by LEHCEBs (c, d) the  $Ti_{49.5}Ni_{50.5}$  samples before corrosion tests (a, c) and after sterilization processing and then the corrosion test in 2 % NaCl solution

Corrosion resistance tests in the 2 % NaCl water solution and sterilizing processing in the water-steam mixed medium ( $T_{ster}=393$  K, pressure by 4 atm.) of the medical TiNi implants modified by LEHCEBs (Fig. 5, *c–d*) and nonmodified (Fig. 5, *a–b*) have shown that the surface modified implants revealed higher corrosion stability comparing with the non-modified ones.

#### 4. Conclusion

Thus, our results shows that pulsed melting with usage of the LEHCEBs of the "film – substrate" systems with different alloying elements (Ti, Zr, Pd) results in formation of alloyed subsurface layers by  $2\div 2.5$  μm in thickness differs from the bulk material by the following: 1) high concentration of an alloying element (10÷20 at.%); 2) higher (in 5 times) value of hardness; 3) improving of corrosion stability and protecting from sterilization impact.

#### 5. Acknowledgement

The authors are grateful to Yu.P. Mironov for assistance in carrying out the X-Ray investigations.

The study was supported by Siberian Branch of Russian Academy of Sciences (RAS, the project No. 91) and Presidium of RAS (the project No. 12.7).

#### References

- [1] C. Shih, S. Lin, Y. Chen, Y. Su, S. Lai, G. Wu, C. Kwok, K. Chung, *J. Biomed. Mater. Res.* 52, 395 (2000).
- [2] L.L. Meisner, V.P. Sivokha, *Phys. Met.&Metallogr.* 88, 572 (1999).
- [3] V.P. Sivokha, L.L. Meisner, *Phys. B* 296, 329 (2001).
- [4] L.L. Meisner, A.I. Lotkov, V.P. Sivokha, A.I. Turova, E.G. Barmina, *Phys.&Chem. obrab. mater.* 1, 78 (2003).
- [5] L.L. Meisner, V.P. Sivokha, A.I. Lotkov, E.G. Barmina, *Phys.&Chem. obrab. mater.* 1, 78 (2006).
- [6] C. Blanco-Pinzon, Z. Liu, K. Voisey, F.A. Bonilla, P. Skeldon, and G.E. Thompson, *Corros. Sci.* 47, 1251 (2005).
- [7] C.W. Draper, L.S Meyer, D.C. Jacobson, L. Buene, J.M. Poate, *Thin Solid Films.* 75, 237 (1981).
- [8] M.Pout (ed.), *Surface modification and alloying of materials by laser, ion and electron beams*, Moscow, Metallurgia, 1987, 424.
- [9] T.J. Renk, R.G. Buchheit, N.R. Sorensen, and D. Cowell, *Phys. plasmas*, 5, 5 (1998).
- [10] L.L. Meisner, V.P. Sivokha, A.I. Lotkov, L.S. Derevyagina, *Phys. B*, 307, 251 (2001).
- [11] L.L. Meisner, V.P. Sivokha, A.I. Lotkov, E.G. Barmina, *J. de Physique IV. France*, 112, 663(2003).
- [12] L.L. Meisner, A.I. Lotkov, S.G. Psachje, E.G. Barmina, V.P. Rotshtein, K.V. Karlik, A.B. Markov, in *Proc. 7<sup>th</sup> Int. Conf. on Modification of Materials with Particle Beams and Plasma Flows*, 2004. pp. 285–288.
- [13] I.I. Kornilov, O.K. Belousov, E.V. Kachur, *Titanium Nikelid and other shape memory alloys*, Moscow, Nauka, 1977, 180.