Effect of the Pulsed Electron Beam Melting on a Chemical Composition and Surface Layer Microstructure of the Tini Alloy[1]

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Abstract – Investigation results of elemental composition, structural-phase conditions and surface morphology behavior of the thin surface layers of the TiNi-based alloys modified with the pulsed electron beam melting are presented in the paper. The low-energy (~ 30keV) high current (~ 30 kA) electron beam (3–10 J/cm^2) pulsed with 2–3 μs in time length have been used. An irradiation treatment was carried out in an argon atmosphere (~ 10^{-4} torr) at different contents of carbon and oxygen impurities in a residual atmosphere.

Correlation between the subsurface layers elemental composition of the $Ti_{49.5}Ni_{50.5}$ alloy and surface treatment conditions (electrolytical polished and irradiated) is shown.

1. Introduction

Investigation of the surface layers properties of the TiNi-based alloys has the peculiarity due to a special martensite relief formed when the alloys reveal superelasticity or a shape memory effect. The reason for that phenomenon are the martensite phase transformations of the high-temperature B2 phase into the B19′ martensite phase accompanying a global morphology changing, uniformity failure, crack formation and, at last, degradation of a shape memory and superelasticity properties.

While the martensite phase transformations and the inelastic properties associated to them for the TiNi-based alloys are investigated mostly [1, 2], than an elemental composition, physical and chemical properties of the TiNi surface layers only start to be developed [3].

Next aspect related to a role of a solid state surface condition is a surface and thin surface layers modification by the ion and/or electron beams irradiation technique. This investigation area is practically unexplored regarding to the TiNi-based alloys. Investigation of the modified superficial layers of these alloys has additional significance in connection with a wide application range of them.

Influence of a surface modification with a pulsed low-energy high-current electron beam irradiation and this ones combined with the ion implantation on the elemental composition and a structural condition of the high-temperature B2 phase of the $Ti_{49.5}Ni_{50.5}$ is studied in the work.

2. Experimental

The investigated $Ti_{49.5}Ni_{50.5}$ alloy was prepared from iodide titanium and nickel of grade NO using sixfold arc remelting. Samples (1×15×15) mm^3 in size for X-ray diffraction and AES analysis were prepared.

Before the measurements, the samples were annealed at 1073 K for 1 h in vacuum higher than 10^{-3} Pa and then furnace cooled. The surface of the samples was etched electrolytically using a solution containing 90% acetic acid and 10% $HClO_4$.

The surfaces of the samples for modification by the electron and ion beam were ground by diamond ink and then electrolytically polished. The phase composition of the alloys were studied by X-ray diffraction using a DRON-2.0 diffractometer. The temperatures of martensitic transformations (MT) were determined from the temperature dependence of the electrical resistivity of the alloy.

The low-energy (~ 30keV) high current (~ 30 kA) electron beam (LEHCEB) (3–10 J/cm^2) pulsed with 2–3 μs in time length have been used. An irradiation treatment was carried out in an argon atmosphere (~ 10^{-4} mmHg) at different contents in a residual atmosphere of carbon and oxygen impurities.

After that one part of the $Ti_{49.5}Ni_{50.5}$ samples modified with LEHCEB technique were ion implanted. Ion implantation was carried out with the repetitively pulsed regime using the ion sources DIANA-II.

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The $Ti_{49.5}Ni_{50.5}$ samples were implanted with Cu^+ and Ti^+ ions. The energy of the ions was equal to 60 keV. The incident doses were equal to $1.4 \cdot 10^{17}$ cm^{-2} for Cu and $1 \cdot 10^{17}$ cm^{-2} for Ti. The temperature of the implanted samples did not exceed 373–424 K.

3. Experimental Results and Discussion

It was found that it can divide the outer and inner subsurface layers of the nonmodified and ion– or electron beams modified $Ti_{49.5}Ni_{50.5}$ samples on the base of their chemical composition within these layers.

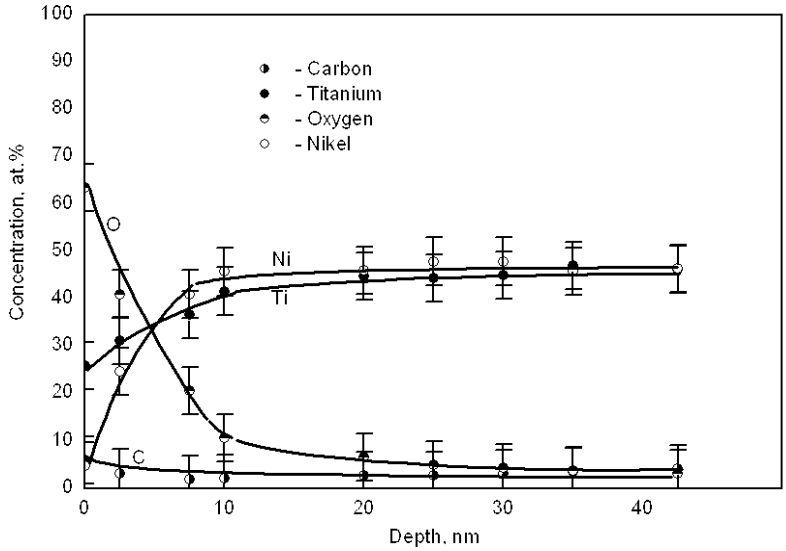

Fig. 1. A typical depth profile of $Ti_{49.5}Ni_{50.5}$ sample electrolytical polished. The oxide film thickness defined at the point when the oxygen concentration drops by factor of a two is ≤ 10 nm

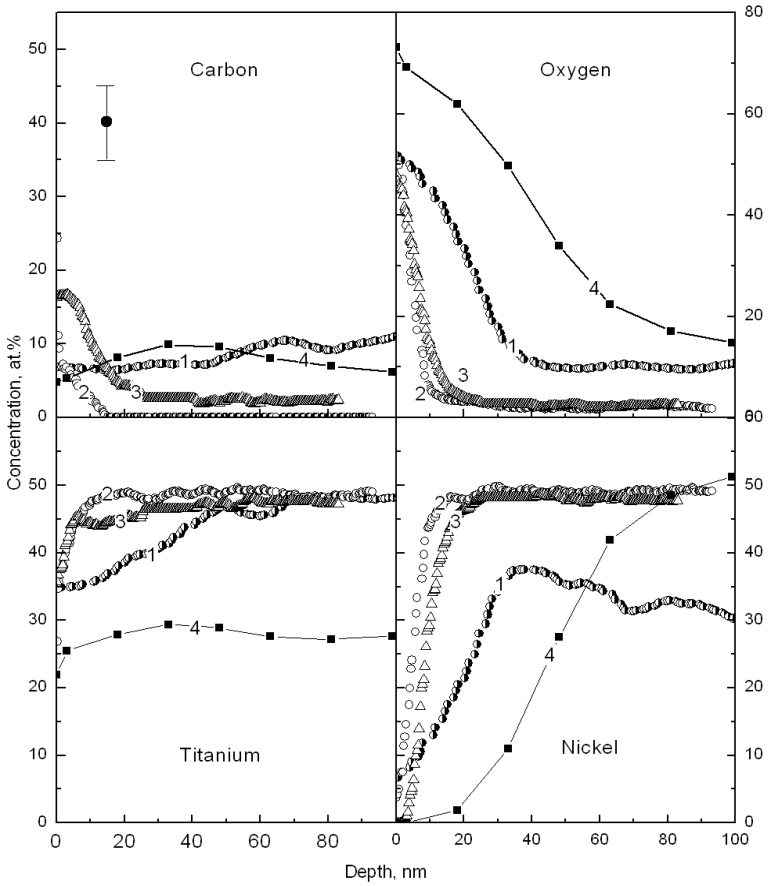

Fig. 2. A depth profiles of $Ti_{49.5}Ni_{50.5}$ samples: curves *1* (in all layers) – surface modification with a low-energy high-current electron beams (LEHCEB) and a high vacuum (~ $5 \cdot 10^{-7}$ mmHg) in the chamber; curves *2* – LEHCEB + the low vacuum (~ 10^{-5}mmHg); curves *3* – LEHCEB (~ $5 \cdot 10^{-7}$ mmHg) + High dozen ion implantation (HDII) with D(Ti) = $1.4 \cdot 10^{17}$ cm^{-2}; curves *4* – HDII with D(Cu) = $2.1 \cdot 10^{17}$$cm^{-2}$ and then D(Ti) = $1.0 \cdot 10^{17}$$cm^{-2}$

So, there is the only subsurface layer for the nonmodified (electrolytical polished) $Ti_{49.5}Ni_{50.5}$ samples characterized by high concentration of oxygen (> 60 at.%) and non-equilibrium Ti/Ni ratio. A depth profiles of $Ti_{49.5}Ni_{50.5}$ samples: curves *1* (in all layers) – surface modification with a low-energy high-current electron beams (LEHCEB) and a high vacuum ($\sim 5\times10^{-7}$ mmHg) in the chamber; curves *2* – LEHCEB + the low vacuum ($\sim 10^{-5}$ mmHg); curves *3* – LEHCEB ($\sim 5\times10^{-7}$ mmHg) + High dozen ion implantation (HDII) with $D(Ti) = 1.4\cdot10^{17}$ cm^{-2}; curves *4* – HDII with $D(Cu) = 2.1\cdot10^{17}$ cm^{-2} and then $D(Ti) = 1.0\cdot10^{17}$ cm^{-2}.

Depth of this layer is about 10–15 nm (Fig. 1). It was revealed that after the electron beam influence a distribution of the main elemental composition of the $Ti_{49.5}N$. Fig. 2 illustrates a depth profiles of $Ti_{49.5}Ni_{50.5}$ samples processed with different surface treatment. In all layers curves *1* correspond to surface modification with a low-energy high-current electron beams (LEHCEB) and a high vacuum ($\sim 5\times10^{-7}$ mmHg) in the chamber; curves *2* – the same LEHCEB treatment with the low vacuum ($\sim 10^{-5}$ mmHg) in the chamber; curves *3* – the LEHCEB ($\sim 5\times10^{-7}$ mmHg) modification and then a high dozen ion implantation (HDII) with $D(Ti) = 1.4\cdot10^{17}$ cm^{-2}; curves *4* – HDII with $D(Cu) = 2.1\cdot10^{17}$ cm^{-2} and then $D(Ti) = 1.0\cdot10^{17}$ cm^{-2}. It is seen that the controlled distribution of the Ti/Ni ratio coupled with an Oxigen and/or Carbon concentration can be reached within the subsurface layers of the $Ti_{49.5}Ni_{50.5}$ samples. Thickness of these layers depends on the kind and consequences of the irradiation surface treatment. For example, thickness of the ion–modified layer with different concentration of the main alloy components (Ti and Ni) equals to ~ 100 nm, whereas these ones of the electron-modified layer vary from ~ 5 nm up to ~ 400 nm.

The important result achieved in the study is the opportunity of controllable formation of the Ni-free outer and low Ni–content inner subsurface layers after the electron– and ion irradiation of the $Ti_{49.5}Ni_{50.5}$ samples. The nature of such layers formation is caused with distribution of main alloy components Ti and Ni

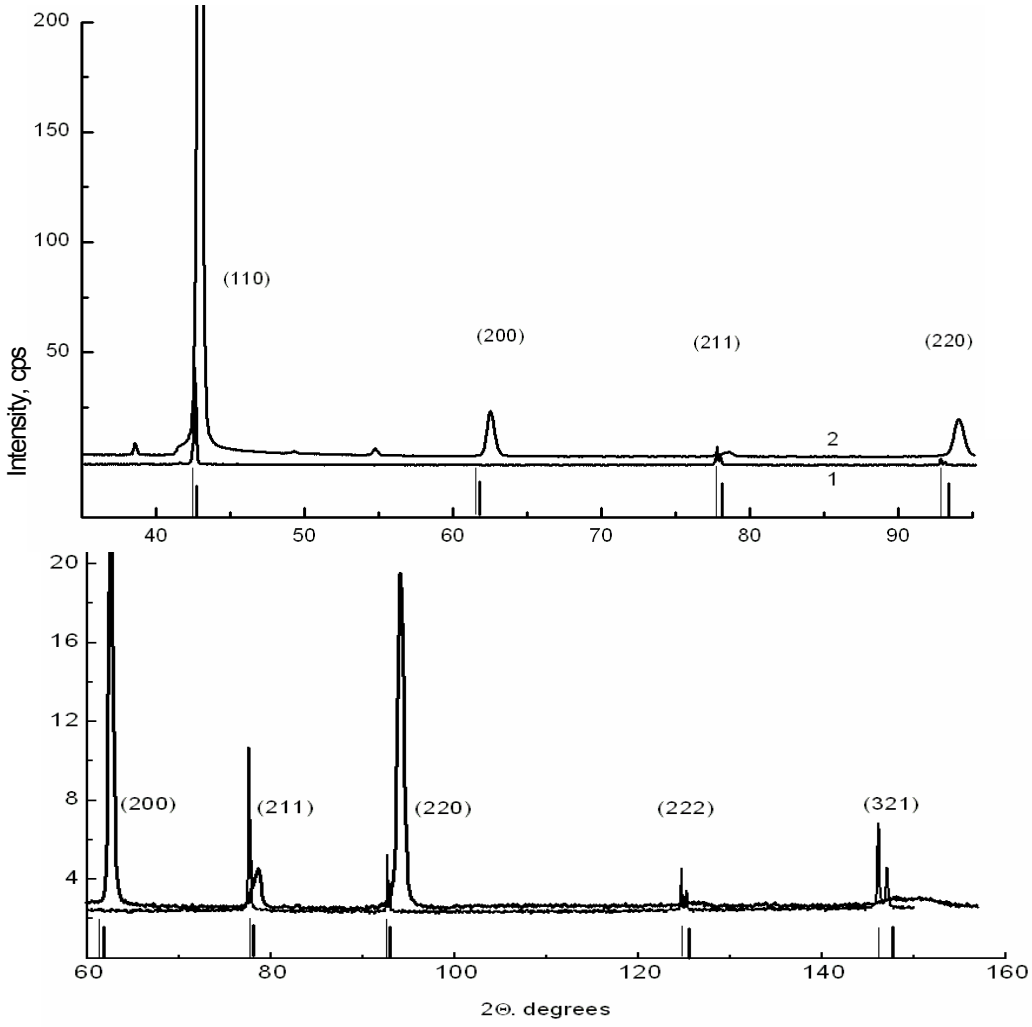

Fig. 3. The typical X-ray diffraction patterns of the initial (1) and distorted (2) B2 phase conditions. Nomographic charts (straight lines at the bottom of the layers) calculated using the experimental B2 lattice parameters

due to their interaction with nonequilibrium defects system consisting of a vacancies, basically. Well known that above crystal defects system is induced by the radiation and distributing within the outer thin surface layer, mainly, on the Ni-sublattice [4]. In this case, the Ni-atoms become most mobile and start to move in the opposite directions to this ones for the vacancies moving, that is, to the core of the sample. All of that lead to the formation the Ni-free or low Ni-content subsurface layers. The thickness of such layers almost three times exceeds thickness of a native oxide film on the TiNi-based alloy.

The X-ray analysis have shown that in the layers, modified by the pulsed electron beam processing, the special microstructural condition is formed. The atomic crystal structure of these layers corresponds to the high-temperature B2 structure with the smaller lattice parameter (a = 3.0050±0.0005 Å), than this one of the initial B2 phase (a = 3.0129±0.0005 Å). Additionally, this new B2-phase is characterized by a significant lattice distortions, small coherent-scattering regions (about 30 nm) and a high internal stress. The typical X-ray diffraction pattern of the distorted B2 phase characterized the electron-modified layer of the $Ti_{49.5}Ni_{50.5}$ alloy is shown in Fig. 3. The thickness of such layer achieves 4÷5 μm.

Thus, it is shown that the electron and ion irradiation surface treatment results in a surface and subsurface layers modification including a drastically changing the elemental composition and structural-phase condition of the TiNi-based alloy. Thickness of the modified layer can achieve from ~10 nm up to ~400 nm depending on treatment conditions.

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