

ISSN 1822-508X



4rd International Conference

**RADIATION INTERACTION
WITH MATERIAL AND ITS USE
IN TECHNOLOGIES 2012**

Program and materials

**Kaunas, Lithuania
May 14-17, 2012**

KAUNAS UNIVERSITY OF TECHNOLOGY
VYTAUTAS MAGNUS UNIVERSITY
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HYDROGEN ENERGY ASSOCIATION

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SHAPE MEMORY EFFECT IN TiNi ALLOY

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Abstract

This paper reports the application of an nitrogen ion implantation for modification of a shape memory alloy. The surface characterization of equiatomic TiNi alloy was performed with the assistance of transmission electron microscopy techniques and the modifications of the phase composition before and after irradiation are studied at the room and martensitic transformation temperatures by X-ray diffraction methods. We investigated the sequence of transformations for the initial and surface-modified materials. Experimental results of near-surface-layers in ion-implanted TNii alloy are discussed in this paper.

Keywords: *shape memory alloy, implantation, modification.*

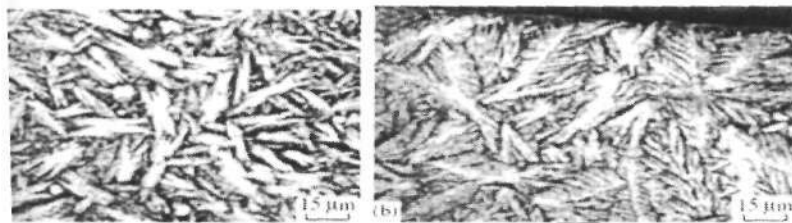
The application of high-dose intense implantation leads to an increase in the ion (mainly N ion) penetration depth; intensified scattering of the surface layer; a shift in the maximum, concentration, and shape of the concentration profile; and many other processes that are weakly pronounced during low-intensity ion implantation at low doses (several units of atomic processes) of implanted ions [1-3]. On the other hand, TiNi-based alloys belong to the group of materials in which a high-temperature phase with a B₂ structure undergoes a shear or martensitic phase transformation as the temperature changes or a stress is applied. The atomic restructuring in TiNi-based alloys is accompanied by both martensitic anelasticity effects and a change in their surface state, which is caused by the complex structure of the martensite phase in them [4-6]. As a result, a developed martensitic relief with a large number of various interfaces appears, which should affect both the electrochemical and corrosion properties and the plasticity and strength properties of these materials. As a method of surface alloying, ion implantation of a surface can strongly affect the structural parameters and stability of the B₂ phase in the near-surface layers and, hence, the following set of its properties: the martensite transformation temperature, the martensite anelasticity parameters, the shape memory effect (SME), and superplasticity. As a result, it can change the deformation relief, the cracking conditions, and the electrochemical and corrosion properties [6]. Therefore, double implantation of N and Ni ions into TiNi is of particular interest, since the implantation of Ni ions changes the equiatomic composition of the alloy and, in combination with N ions, hardens the surface layer and, correspondingly, modifies the physicomechanical and chemical properties [4].

In this article the investigations were carried out on an equiatomic NiTi (Ti-50Ni) martensitic form has been used in over investigation. Samples (5.4x0.25 mm) were annealed at 573 K for 30 min in vacuum and then cooled in the furnace. Nitrogen ion implantation (at several doses: $1 \times 10^{17} \text{ cm}^{-2}$, 10^{18} cm^{-2} and $2 \times 10^{18} \text{ cm}^{-2}$, at energy 50-65 keV) was carried out using a semi-industrial implanter IMJON (IFTR PAS, Warsaw).

Differential scanning calorimetry (DSC, TA Instruments) was used to characterize the transformation sequence and transformation temperatures for initial and surface-modified materials. Measurements were carried out in vacuum atmosphere with a cooling/heating rate of $20^\circ\text{C}/\text{min}$.

Auger electron spectroscopy on a PHI-660 (Perkin-Elmer) device, scanning electron microscopy on a Selm (Sumy, Ukraine) microscope equipped with EDS and WDS microanalyses and on a Perkin-Elmer scanning electron microscope, and Rutherford backscattering of ions (2.012 MeV proton beams, 1 MeV ^4He ion beams). Rutherford backscattering spectra were analyzed using the standard software packages to construct the depth profiles of nitrogen.

Figure 1 shows optical microscopy data. They demonstrate a typical martensitic structure and changes in the martensitic structure after implantation.



1. Optical micrographs of (a) a TiNi alloy with a martensitic structure and SME: (a) before and (b) after ion implantation

The surface layer of the implanted sample has a significant concentration of nitrogen and oxygen and the characteristic peeling away is observed in the surface of TiNi implanted by nitrogen.

Figure 2 shows the results of loading and unloading (at loads of 4 and 7 N) of samples before and after implantation at doses of $5 \times 10^{17} - 10^{18} \text{ cm}^{-2}$. The samples implanted by N^+ ions are seen to have a higher (by 15-20%) SME than the initial samples. The changes in the SME demonstrate that the aged TiNi alloy exhibits an indentation with a higher hardness after heating as a result of healing to 75°C . In other words, all mechanical changes of the SME and mechanical properties (hardness) are interrelated with the elemental composition and micro-structure of the material.

When analyzing the profile of N^+ ions in TiNi it was found that the nitrogen concentration has a double-humped shape: one concentration maximum is located near

the surface (the maximum concentration is about 36 at.%) and the second peak is located at a depth of more than 130-150 nm (and has a lower concentration 27 at.%). In the valley between the two nitrogen concentration maxima, the concentration of Ni⁺ ions is maximal (about 20 at.%).

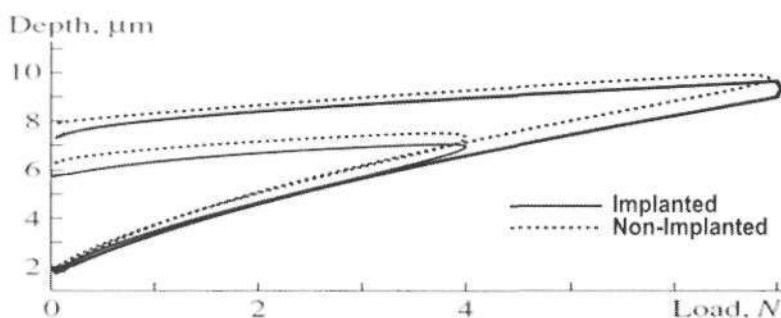


Fig. 2. Indentation curves for implanted and unimplanted TiNi samples exhibiting SME

DSC measurements were carried out a temperature range from -50°C to $+150^{\circ}\text{C}$ was scanned at a rate of $20^{\circ}\text{C}/\text{min}$ during cooling and heating. DSC cooling/heating curves, the NiTi alloy transforms in two steps showing two peaks on the DSC curve in the cooling direction. The first DSC peak correlates with the transformation from the austenite with a cubic structure (B_2 -phase) to the R-phase with a rhombohedral one. The second DSC peak correlates with the transformation from the R-phase to the martensite (M) with a monoclinic structure ($B_{19'}$ -phase). Two-step martensite phase transition from high temperature was observed for the NiTi alloys after the thermo-mechanical treatment. The one-step but composed transition took place during the heating process. The endothermic peak during the heating process resulted in the transition of the martensite to the austenite phase. The peak in the heating direction corresponds to the austenite (B_2 -phase) with $t_{\text{start}} = 51.6^{\circ}\text{C}$, $t_{\text{finish}} = 62.3^{\circ}\text{C}$ for the virgin alloy and with $t_{\text{start}} = 52.5^{\circ}\text{C}$, $t_{\text{finish}} = 64^{\circ}\text{C}$ for the ion-implanted one. The subscript 'start' denotes the onset temperature at which the phase transformation starts, and the 'finish' the temperature at which the phase transformation finishes. The two peaks in the cooling direction corresponding to the R-phase and the martensite $B_{19'}$ -phase were determined to have transformation temperatures, respectively: $t_{\text{start}} = 45.1^{\circ}\text{C}$, $t_{\text{finish}} = 37.8^{\circ}\text{C}$, $t_{\text{start}} = 19^{\circ}\text{C}$, $t_{\text{finish}} = 1^{\circ}\text{C}$ for the virgin alloy and $t_{\text{start}} = 43.3^{\circ}\text{C}$, $t_{\text{finish}} = 37.4^{\circ}\text{C}$, $t_{\text{start}} = 24.6^{\circ}\text{C}$, $t_{\text{finish}} = 11.6^{\circ}\text{C}$ for an ion-implanted alloy.

The appearance of austenite phase (crystalline, nanocrystalline and/or amorphous-like) may be related to structural changes in the NiTi alloy during the ion implantation process and to high temperature of target. Appearance of the R-phase, similar to the results obtained for annealed materials, may be induced by high temperature of target. An increase of temperature in the material results in an increasing fraction of the B_2 -phase. The diffraction

patterns of this B_{19} -phase do not vary up to 65 °C. Above this temperature an increasing fraction of the B_2 -phase and a distinctly decreasing fraction of the B_{19} one were observed. The $B_{19} \rightarrow B_2$ phase transformation finishes above a temperature of 80 °C. The X-ray diffraction patterns obtained for the highest temperatures (from 80 °C to 150 °C) contain only reflections from the B_2 -phase. Lowering the temperature up to about 41 °C, besides still existing B_2 -phase, the R-phase appears. The $R \rightarrow B_{19}$ -phase transformation starts from a temperature of 25 °C and finishes about 25 °C. Along with the decreasing temperature, besides the dominating B_{19} -phase, a small amount of the B_2 -phase was detected. Such phase composition was also observed for the material at 20 °C on the start and finish of the second thermal cycle. Structure of this diffraction peak may testify that still some amount of the amorphised and/or nanocrystalline B_2 -phase is present in the alloy.

Conclusions. The sequential implantation of N^+ ions into nitinol (TiNi) leads to the formation of a complex depth profile of the nitrogen concentration, which is caused by the rejection of nitrogen ions from the region of the maximum N^+ ion losses (i.e., the region of the maximum N^+ ion concentration) to the region of residual tensile stresses. The SME changes because of the formation of nitrogen and carbon (carbonitride) layers as a result of N^+ implantation and because of a change in the concentrations of Ti and Ni atoms due to the sputtering of Ni atoms, which is accompanied by a change in the martensite transformation temperature. Both the unimplanted and ion-implanted NiTi alloys transform in two steps ($B_2 \rightarrow R \rightarrow B_{19}$) in the cooling direction and one-step transition ($B_{19} \rightarrow B_2$) in the heating process.

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ISSN 1822-508X

SL 344. 2012-05-04. 40,75 leidyb. apsk. I. Tiražas 210 egz.

Kaina sutartinė. Užsakymas 478.

Išleido leidykla „Technologija“, K. Donelaičio g. 73, 44029 Kaunas
Spausdino leidyklos „Technologija“ spaustuvė, Studentų g. 54, 51424 Kaunas

Bratushka, S. N. Shape memory effect in TiNi alloy [Текст] / S. N. Bratushka // Radiation interaction with material and its use in technologies 2012 : 4rd International Conference (May 14-17). - Kaunas: Kaunas university of technology, 2012. - P. 290-293.