

# Formation of Nanosized Intermetallic Phases in Ni-Ti System upon Ion Implantation

I.A. Kurzina, I.A. Bozhko, M.P. Kalashnikov, Yu.P. Sharkeev,\* E.V. Kozlov

*Tomsk State University of Architecture and Building, 2 Solyanaya pl., Tomsk, 634003, Russia,  
Phone: +7(3822)65-42-65, Fax: +7(3822)65-42-63, E-mail: kurzina99@mail.ru*

*\* Institute of Strength Physics and Materials Science of RAS,  
2/1 Academicheskii pr., Tomsk, 634021, Russia*

**Abstract** – Results of an experimental research of a microstructure, phase composition and mechanical properties of the surface ion-alloyed layers of nickel formed in conditions of high-intensity titanium ion implantation are presented. It is established, that ion implantation of the nickel allows to form finely-dispersed intermetallic phases ( $\text{Ni}_3\text{Ti}$ ,  $\text{NiTi}$ ,  $\text{NiTi}_2$ ) and solid solution Ti in Ni in surface layers thickness up to 1600 nm. It is shown, that the intermetallic phases formed in ion-alloyed surface layers of nickel are nanocrystalline; the average size of phases grains is 40 nm. It is established, that the nickel surface layers alloyed by titanium ions has higher mechanical characteristics in comparison with an initial material of a target.

## 1. Introduction

The progress of today's industrial development largely depends on how the problem of reliability, efficiency, and service life of components and mechanisms is solved. Many of the operating parameters of materials depend to a large extent on the state of the surface layer of the material they are made of. Ion implantation is one of the ways to improve mechanical and physicochemical properties of material surfaces (higher wear resistance, corrosion resistance, resistance to radiation damage, etc.) [1]. An ion beam treatment of surface layers of materials gives rise to formation of high-concentration solid solutions, nanosized interstitial alloy and non-equilibrium phases, and intermetallic compounds. It also ensures high-intensity concentrational mixing, formation of highly defective structures, etc. Within the recent time there has been a great interest in applying ion implantation to synthesize intermetallic phases, in particular, Ni-Al, Ti-Al, Ti-Ni systems and etc. The urgency and topicality of this problem are due to the unique physicochemical properties of intermetallic compounds of these systems [2]. Alongside their sufficient ductility, they maintain their structure and strength under high temperature impacts, exhibit good corrosion and friction performance, where they are advantageous over conventional materials. In [3, 4], it was demonstrated that it is possible to significantly improve the physical-

mechanical properties of nickel and titanium surface layers due to formation of intermetallic phases in a metallic matrix via high-intensity ion implantation.

The high intensity ion implantation allows obtaining the ion beam-alloyed layers in the target materials with the thickness greater than that of the ion projected range. The increase of the ion-alloyed surface layer thickness at the high intensity ion implantation can be achieved by the high-rate of implanted-ion dose accumulation, the controlled heating of the target by the ion beam and the high rate of alloyed impurities diffusion. The above mentioned advantages favor to produce modified surface properties with thickness several micrometers containing the intermetallic compounds.

It is known that under ion implantation at chemical reactions temperatures, the formation of new phases occurs according to the phase diagram. Properties, structure and morphology of surface layers are controlled by a set of physical conditions of ion implantation and, depending on these, vary within a wide range. In this connection, an urgent task is to identify regular physicochemical features of formation of ion-doped metal layers containing nanosized intermetallic phases under high-intensity ion implantation treatment.

The aim of the present paper is to investigate the phase composition, structural state and mechanical properties of the nickel surface layers formed by ion implantation of the titanium ions.

## 2. Experimental

The material used as target for ion implantation was pure monocrystal nickel. The nickel samples were implanted by titanium ions. The high intensity ion implantation was carried out using the "Raduga-5" source based on continuous-discharge vacuum arc plasma generation at an accelerating voltage of 20 kV. There were carried out two series of experiments of ion implantation that differ in the distance from a source, temperature of a target and, correspondingly, the dose of irradiated ions (Table 1).

Table 1. Conditions for high-intensity implantation of titanium ions into nickel samples

Regime	Accelerating voltage, kV	Samples temperature at ion implantation, K	Distance between samples and ion source, m	Ion irradiation period, min	Dose of irradiated ions, $\text{ion}\cdot\text{cm}^{-2}$
1	20	850	0.68	120	$0.3\cdot 10^{18}$
2	20	1000	0.43	120	$2.9\cdot 10^{18}$

The concentration profiles of elements across the nickel surface layers of the implanted materials were determined using the methods of Auger electron spectrometry (AES). The phase composition and structural state were investigated by X-ray diffraction (XRD) method and transmission electron microscopy (TEM). Transmission electron microscopy investigations were performed on a Tesla BS-540 electron microscope. XRD spectra were recorded on a diffractometer "DRON-3" using  $\text{FeK}_\alpha$  radiation.

The microhardness of the samples was investigated with a CSEM Nano Hardness Tester NHT-S-AX-OOOX (Switzerland) with the use of Vickers indenters. The loads on the indenter varied from 0.015 to 0.28 N. The tribological characteristics were studied in air with a CSEM High Temperature Tribometer THT-S-AXOOO instrument (Switzerland) in a pin-on-disk configuration.

### 3. Results and discussion

Table 2. summarizes the main characteristics of ion-alloyed layers of nickel, which were obtained with TEM, XRD, and Auger spectroscopy. Fig. 1 shows the element concentration distribution with respect to the depth of the nickel implanted with titanium ions. As follows from the AES concentration profiles, an increase in the implantation dose results in an increase in the thickness of the ion-doped layers; the layer thickness is equal to 600 nm upon implantation in regime 1 and 1600 nm upon regime 2 (Table 2, Fig. 1).

Table 2. Main characteristics of nickel surface layers implanted with titanium ions

Regime		1	2
Thickness of ion-alloyed layer, nm		600	1600
Phase composition	TEM	$\text{Ni}_3\text{Ti}$ , $\text{NiTi}$ , $\text{NiTi}_2$ , solid solution Ti in Ni, $\text{TiC}$ , $\text{TiO}_2$ (rutile, orthorhombic), $\text{NiTiO}_3$	$\text{Ni}_3\text{Ti}$ , $\text{NiTi}$ (monoclinic, cubic), $\text{NiTi}_2$ , solid solution Ti in Ni, $\text{NiC}$ , $\text{TiC}$ , $\text{TiO}$ , $\text{T}_2\text{O}$ , $\text{TiO}_2$ (rutile, orthorhombic, anatase)
	XRD	$\text{Ni}_3\text{Ti}$ , $\text{NiTi}$ , $\text{NiTi}_2$ , $\text{TiO}_2$ (rutile, orthorhombic), $\text{TiC}$	$\text{Ni}_3\text{Ti}$ , $\text{NiTi}$ , $\text{TiO}$ , $\text{Ti}_2\text{O}$ , $\text{TiO}_2$ (rutile, orthorhombic), $\text{Ti}_3\text{O}_5$
Average size of phases, nm		35	40

A maximum titanium content (60 at. %) in the nickel surface layer implanted with dose  $0.3\cdot 10^{18}$   $\text{ion}\cdot\text{cm}^{-2}$ , occurs at a depth interval of 100–350 nm from the irradiated surface. The Ti con-

tent at depths of more than 500 nm does not exceed 5 at. %. An increase in the implantation dose up to  $2.9\cdot 10^{18}$   $\text{ion}\cdot\text{cm}^{-2}$  (fig. 1, b) leads to moving of the maximum Ti content (60 at. %) to deeper regions (interval 200–600 nm). As the temperature and the dose of implantation increase, the titanium concentration profile falls off more smoothly with an increase in the distance from the irradiated surface due to the diffusion processes. Thus, the titanium contents in materials implanted according to regimes 2 are lower than 55 at. % at depths of 1500 nm and more (Fig. 1, b).

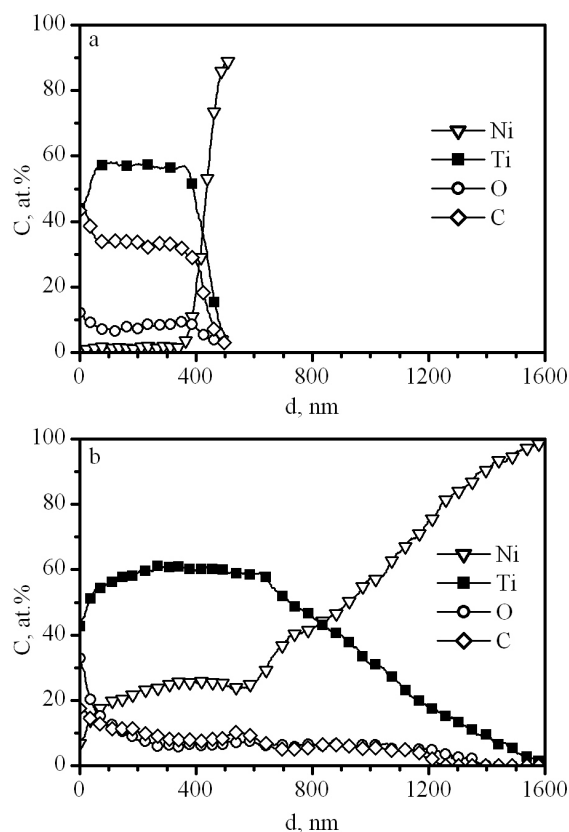


Fig. 1. Concentration profiles of the nickel surface layers implanted with titanium ions in regime 1 (a) and regime 2 (b)

The modified nickel layers contain titanium ions and also oxygen and carbon impurities, which come from a residual atmosphere of a vacuum system and were adsorbed by a target surface in the course of ion implantation. The maximum oxygen and carbon concentration ( $\sim 30$  at. %) exists at depths interval 100–400 nm. The oxygen content is not exceeding 10 at. % at depth more then 50 nm. As the same time, the nickel sample implanted at regime 2 has less content of oxygen and carbon; their contents in materials are lower than 10 at. % at depths of 100 nm and more from irradiates surface (Fig. 1, b).

The X-Ray diffraction patterns of nickel samples implanted with titanium ions at 1 and 2 regimes are presented in Fig. 2 (the peaks of pure nickel are not shown on fig. 2 due to their high intensity compare to

formed phases). The peaks of intermetallic phases of Ti-Ni system ( $\text{Ni}_3\text{Ti}$  (structure  $\text{D0}_{24}$ ) and  $\text{NiTi}$  (structure  $\text{B}_2$ ) are presented on XRD patterns (Fig. 2, Table 2). In addition to intermetallic phases, it was established the  $\text{NiTi}_2$  compound formation (fig. 2, b, table 2) in nickel surface layers implanted with dose  $0.3 \cdot 10^{18} \text{ ion} \cdot \text{cm}^{-2}$ .

The high concentration of penetrated impurities and temperature of irradiation led to oxide and carbide phases formation. Apart from the aforementioned intermetallic phases, we also observed the formation of the titanium oxides with different stoichiometric compositions ( $\text{Ti}_2\text{O}$ ,  $\text{TiO}$ ,  $\text{TiO}_2$ ,  $\text{Ti}_3\text{O}_5$ ) and also the titanium carbide in sample implanted at regime 2 (Table 2). The ratio and chemical composition of titanium oxides depend on implantation regimes (Table 2).

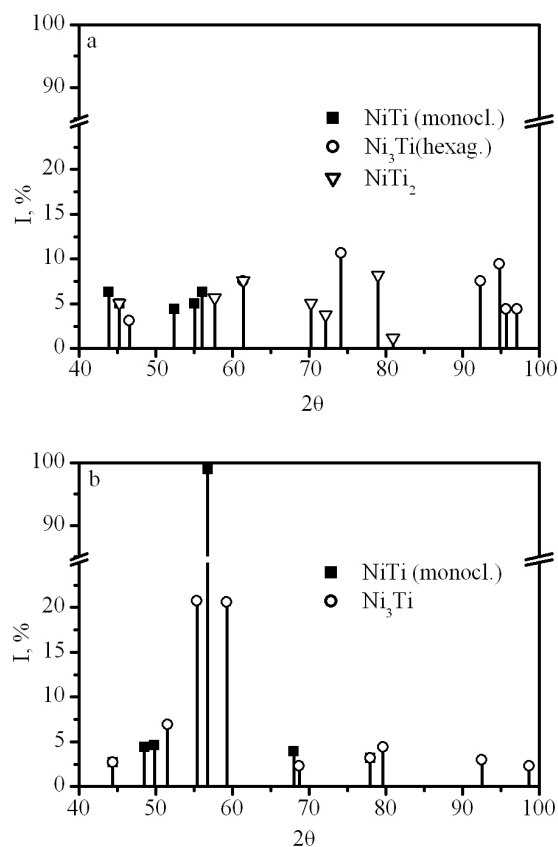


Fig. 2. X-ray diffraction patterns of Ni implanted with Ti ions in regime 1 (a) and regime 2 (b)

Figs 3 and 4 show the electron microscopy bright- and dark-field images and microdiffraction patterns from the surface ion-alloyed layer of nickel irradiated with regimes 1 and 2 correspondingly. The TEM investigation of microstructure and phase composition of implanted nickel (Fig. 3 and 4) demonstrated that  $\text{Ni}_3\text{Ti}$ ,  $\text{NiTi}$ ,  $\text{NiTi}_2$  phases and solid solution of Ti into Ni are formed in the surface layers. The microdiffraction pattern of the ion-alloyed nickel surface layer implanted in regimes 1 and 2 (Fig. 3, b, 4, b) involves a set of individual Debye

rings, among which the most intense rings correspond to the intermetallic phases  $\text{Ni}_3\text{Ti}$  and  $\text{NiTi}$ . It can be seen from the dark-field images (Fig. 3, 4, c) that, upon implantation the formed particles of the intermetallic phases have nanosizes. The mean size of intermetallic -phase grains is equal to  $\sim 30\text{--}40 \text{ nm}$  (Table 2).

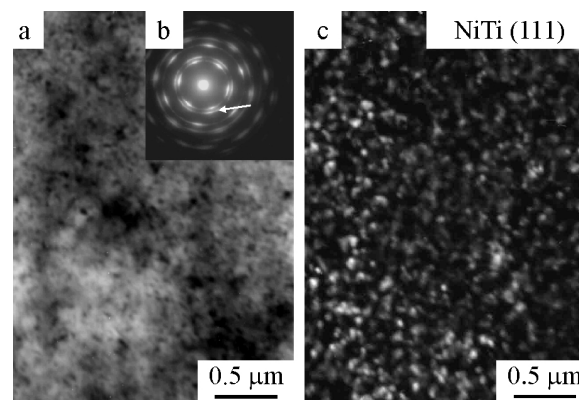


Fig. 3. TEM images of the nickel surface layer implanted with titanium ions in regime 1: a – bright-field image; b – microdiffraction pattern; c – dark-field image

Apart from the intermetallic phases, the formation of the titanium oxides and titanium carbide was observed (Table 2). The different of phases compositions established by TEM and XRD methods can be explained in terms of a less phase's concentration and their irregular localization.

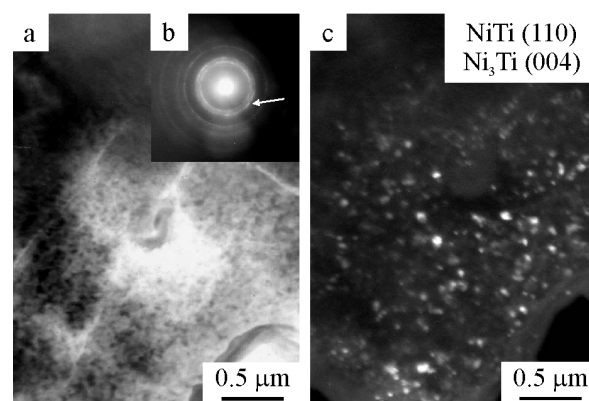


Fig. 4. TEM images of the nickel surface layer implanted with titanium ions in regime 2: a – bright-field image; b – microdiffraction pattern; c – dark-field image

According to the investigation of mechanical properties, the micro-hardness of all the implanted samples at depths to  $2 \mu\text{m}$  is higher than that of initial materials at the same depth. For example, the microhardness of the nickel sample implanted under conditions 2 increases by a factor of 1.5–2 in the surface region  $\sim 1 \mu\text{m}$  thick. The temperature dependences of the wear for the nickel samples indicated that the wears of the ion-alloyed and initial nickel

samples at a temperature of 300 K do not differ substantially. However, an increase in the temperature to 700 K leads to a noticeable increase in the wear of the initial sample by factor of 1.5. By contrast, the wear of the ion-alloyed sample almost does not depend on the temperature.

#### 4. Conclusion

Thus, the high-intensity ion implantation provided by the Raduga-5 source makes it possible to produce implanted layers whose thicknesses large as 1.5  $\mu\text{m}$ . The implantation of titanium ions into nickel results in the formation of nanocrystalline phases of intermetallic compounds ( $\text{Ni}_3\text{Ti}$ ,  $\text{NiTi}$ ),  $\text{NiTi}_2$  phase, titanium oxides and carbide and also a nickel-titanium solid solution of variable composition. The formation of ion-alloyed multiphase layers containing intermetallic phases permits one to improve substantially the mechanical properties of nickel. It

was established that irradiated nickel samples have higher mechanical properties than unimplanted material.

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