Influence of ion implantation on nanoscale intermetallic-phase formation in Ti–Al, Ni–Al and Ni–Ti systems

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Abstract

The objective of this investigation was to study the chemical and phase composition, structure and mechanical properties of titanium and nickel surface layers modified by high-intensity ion implantation with the use of a “Raduga-5”-vacuum-arc ion beam and plasma flow source. Ti samples were irradiated with Al ions, and Ni targets were implanted with Al or Ti ions. It was established that ion implantation in high-intensity mode allows the formation of finely-dispersed (grain size less than 100 nm) intermetallic phases A3B and AB (A=Ti, Ni; B=Al, Ti), as well as solid solutions of composition variable in depth in the surface layer. The localization regions of the intermetallic phases formed over the implanted layer depth were determined. Increasing dose of irradiated ions leads to an increase in the thickness of the ion-alloyed layers up to 3 μm and in the mean size of intermetallic-phase grains. It was shown that high-intensity ion implantation results in a considerable increase of microhardness and wear resistance of the materials. The inference is that the structural and phase state of the ion-alloyed layers affects their mechanical properties.

Keywords: High-intensity ion implantation; Intermetallic nanophases

1. Introduction

Nickel and titanium alloys have been widely used as structural materials in many fields of modern industry. However, the mechanical properties of these alloys can be substantially improved through their surface modification. One of the promising methods for controlling the mechanical, tribological and corrosive properties of metals and alloys is ion implantation [1,2]. The improvement of physical and mechanical properties of implanted materials is associated with the fact that highly concentrated solid solutions, nanosized interstitial phases, intermetallic compounds, etc. are formed in surface layers.

In recent years, the synthesis of intermetallic compounds by ion implantation, in particular Ni–Al [3,4] and Ti–Al [5] system has become a matter of great research interest. The reason is that intermetallic compounds belong to a unique class of materials, which retain their structure up to their melting temperature and possess good mechanical properties [6]. Researchers pay special attention to the possibility of the use of ion implantation for the synthesis of intermetallic phases in nanocrystalline and subnano-crystalline states [4,7]. In these states even at average and low temperatures, intermetallic compounds possess good ductility and even superplasticity while exhibiting higher strength, which makes it possible to improve the mechanical properties of the materials.

Intermetallic structures in the nanocrystalline state in the surface layers of materials can be successfully formed by treating the surface with high-intensity beams of metal ions. The high-intensity ion-implantation mode ensures a high rate of implanted ion dose accumulation, heating the target to the required temperature, and the formation of modified layers as thick as a few micrometers [7,8].

The objective of this work was to compare and determine the common regular features of formation of structural-phase states in surface ion-alloyed layers of Ni and Ti containing nanosized intermetallic phases as a function of the conditions of high-intensity ion implantation and the target properties.
2. Experimental

The materials used as targets for ion implantation were pure polycrystalline nickel and titanium (Russian designation is BT 1-0). The samples were cut by the electro-spark method in the form of plates. Then the samples were subjected to recrystallization annealing for 1 h. at 1073 K in high vacuum. After that the samples were hand ground and electropolished.

The titanium samples were irradiated with aluminum ions (Ti–Al system) and the nickel samples were implanted by aluminum (Ni–Al system) or titanium (Ni–Ti system) ions. The high-intensity ion implantation was carried out using the “Raduga-5” source based on continuous-discharge vacuum-arc plasma generation [4,8,9]. A distinguishing feature of the “Raduga-5” source developed at the Institute of Nuclear Physics at TPU is that it is capable of forming a repetitively pulsed or continuous beam of ions with an energy up to 120 keV from the plasma of a continuous vacuum-arc discharge [8,9]. The main parameters of the implantation regimes are presented in Table 1. Two experimental series of ion implantation for each system were carried out (called respectively: Ti–Al-I, Ti–Al-II; Ni–Al-I, Ni–Al-II; Ni–Ti-I, Ni–Ti-II).

The concentration profiles of elements across the surface layers of the implanted materials were determined using Rutherford backscattering spectrometry (RBS) and Auger electron spectrometry (AES). The structural-phase state of the ion-implanted metal layers was studied with transmission electron microscopy (TEM) using a Tesla BS-540 electron microscope at an accelerating voltage of 120 kV. The phase analysis was carried out at identification of the selected area diffraction (SAD) patterns. The size of formed phases was determined from dark-field images by the secant method. 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 at sample temperatures in the 298–700 K range with a CSEM High Temperature Tribometer THT-S-AXOOOX instrument (Switzerland) in a pin-on-disk configuration. As a pin there was a use of a SiC ceramic sphere 1.5 mm in diameter.

3. Results and discussion

3.1. Elemental composition of ion-alloyed layers

Table 2 summarizes the main characteristics of all the ion-alloyed layers of nickel and titanium which were obtained with TEM, RBS and AES. Fig. 1 shows the element concentration distribution with respect to the depth of the examined specimens of titanium implanted with aluminum ions (regime Ti–Al-II), nickel implanted with aluminum (regime Ni–Al-II) and titanium (regime Ni–Ti-II) ions. As follows from the concentration profiles (Table 2, Fig. 1), the most extensive thickness of modified surface layer was 2600 nm for Ti–Al system, 1000 nm for Ni–Al system and 1600 nm for Ni–Ti system.

The maximum concentration of the penetrated ions in the surface layers of all implanted samples was 60–70 at.%. Nevertheless, the specimens differ in shape of the concentration profiles of penetrated ions (see Fig. 1). For Ni–Al system, the maximum aluminum concentration (60–65 at.%) for two regimes is within the surface itself, while for titanium the maximum Al concentration (60 at.%) is localized at a depth of 350 nm (regime Ti–Al-I) and 1000 nm (regime Ti–Al-II) from the surface. For the case of titanium ions implanted into nickel, the maximum Ti concentration (60 at.%) is observed at a depth 100–300 nm (regime Ni–Ti-I) and 250–600 nm (regime Ni–Ti-II) from the surface. It should be noted, that as the irradiation dose is increased the concentration profile of implanted ions falls off more smoothly with an increase in distance from the irradiated surface due to diffusion processes and the concentration maximum is shifted towards larger depths.

As follows from the concentration profiles, in addition to implanted elements (Al, Ti) the surface layers of the irradiated specimens contained oxygen and carbon impurities adsorbed on the target surface from the residual atmosphere of the vacuum system and mixed into the surface layers by the ion beam [7].

3.2. Structural-phase state of ion-alloyed layers

Microdiffraction analysis of the ion-alloyed titanium specimens demonstrates that the surface layers of all the samples involve the intermetallic phases α2-Ti3Al (the D019 structure) and γ-TiAl (the L12 structure) and also the α phase (solid solution of aluminum in titanium) (Table 2). The bright-field and dark-field images in the corresponding reflections of the diffraction patterns of titanium layers implanted with aluminum ions according to regime Ti–Al-I are displayed in Fig. 2. It can be seen from the dark-field images (Fig. 2c) that, upon implantation in regime Ti–Al-I, the formed particles of intermetallic phases (Ti3Al, TiAl) are nanosized and these grains form conglomerates with a mean size that is equal to 32 and 70 nm, respectively. Increase in the implantation dose results in a change in the SAD patterns of the implanted titanium layers,

### Table 1: Conditions for high-intensity implantation of nickel and titanium samples

<table>
<thead>
<tr>
<th>Target Ion</th>
<th>Implanted Ion</th>
<th>Regimes</th>
<th>Accelerating voltage, kV</th>
<th>Distance between samples and ion source, m</th>
<th>Specimen temperature in ion implantation, K</th>
<th>Ion irradiation period, min</th>
<th>Dose of irradiated ions, ion/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Al</td>
<td>Ti–Al-I</td>
<td>20</td>
<td>0.40</td>
<td>1170</td>
<td>35</td>
<td>6.2·10¹⁷</td>
</tr>
<tr>
<td>Ni</td>
<td>Al</td>
<td>Ni–Al-I</td>
<td>40</td>
<td>0.63</td>
<td>500</td>
<td>20</td>
<td>2.0·10¹⁸</td>
</tr>
<tr>
<td>Ni</td>
<td>Ti</td>
<td>Ni–Ti-I</td>
<td>20</td>
<td>0.68</td>
<td>850</td>
<td>120</td>
<td>0.8·10¹⁸</td>
</tr>
<tr>
<td>Ni</td>
<td>Ti</td>
<td>Ni–Ti-II</td>
<td>0.43</td>
<td></td>
<td>1000</td>
<td>2.9·10¹⁸</td>
<td></td>
</tr>
</tbody>
</table>
primarily due to increase in the mean size of grains of the formed phases. The microdiffraction pattern of the titanium layer implanted with ions according to regime Ti–Al-II is represented by a set of individual point reflections. Examination of the microdiffraction patterns demonstrates that the $\alpha_2$-Ti$_3$Al intermetallic phase is characterized by the 021, 6 $\bar{1}$2 and 212$\bar{2}$ orientation axes. It was detected that the intermetallic phases with mean grain size of 70 nm and their conglomerates with mean size of 584 nm were formed in the ion-alloyed titanium layer (Table 2).

Fig. 3 shows electron microscopy bright- and dark-field images and SAD patterns from the surface layer of nickel implanted by Al ions. Analysis of the microdiffraction pattern (Fig. 3b) demonstrates that a $\gamma$-phase (solid solution of aluminum in nickel), a $\gamma'$-phase (intermetallic Ni$_3$Al) and a $\beta$-phase (intermetallic NiAl) are formed in the surface layer [4]. The intermetallic phases formed in the surface layer of nickel under ion implantation are highly dispersed. Analysis of the dark-field images taken from reflections of the intermetallic phases demonstrated that the average grain size is 24 nm (regime Ni–Al-I) and 38 nm (regime Ni–Al-II) respectively (Table 2). It has to be noted that as for the Ti–Al system, increase in the implantation dose leads to an increase in the mean size of intermetallic-phase grains.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Thickness of ion-alloyed layer, nm</th>
<th>Average size of phases and conglomerates (*), nm</th>
<th>Phase composition</th>
<th>Localization Oxides and carbides depth of intermetallic phase and solid solution (ss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–Al-I</td>
<td>1600</td>
<td>32; 70*</td>
<td>$\gamma$-TiAl (80–450 nm) $\alpha_2$-Ti$_3$Al (80–520 nm) $\alpha$-ss (80–1600 nm)</td>
<td>TiO$_2$ (hexagonal), TiC (cubic), $\gamma$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>Ti–Al-II</td>
<td>2600</td>
<td>70; 584*</td>
<td>$\gamma$-TiAl (400–1250 nm) $\alpha_2$-Ti$_3$Al (400–1600 nm) $\alpha$-ss (400–2600 nm)</td>
<td>TiO$_2$ (anatase, hexagonal, orthorhombic), TiO (monoclinic, hexagonal) $\gamma$- and $\gamma'$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>Ni–Al-I</td>
<td>350</td>
<td>24</td>
<td>$\beta$-NiAl (to 70 nm) $\gamma'$-Ni$_3$Al (to 150 nm) $\gamma$-ss (to 350 nm)</td>
<td>Al$_2$O$_3$ (cubic)</td>
</tr>
<tr>
<td>Ni–Al-II</td>
<td>1000</td>
<td>38</td>
<td>$\beta$-NiAl (to 50 nm) $\beta'$-NiAl (20–40 nm) $\gamma'$-Ni$_3$Al (to 120 nm) $\gamma$-ss (to 1000 nm)</td>
<td></td>
</tr>
<tr>
<td>Ni–Ti-I</td>
<td>600</td>
<td>41</td>
<td>NiTi (to 395 nm) Ni (to 435 nm) Ni$_3$Ti (to 495 nm) ss (to 600 nm)</td>
<td>TiO$_2$ (orthorhombic), TiO$_2$ (hexagonal), Ti$_2$O, TiO (hexagonal)</td>
</tr>
<tr>
<td>Ni–Ti-II</td>
<td>1600</td>
<td>40</td>
<td>NiTi (to 1100 nm) Ni$_3$Ti (to 1300 nm) ss (to 1600 nm)</td>
<td>TiO$_2$ (rutile), TiO$_2$ (anatase), TiO$_2$ (orthorhombic), Ti$_2$O (monoclinic), TiO (hexagonal), TiO (tetra.), TiO (cubic), TiO (monoclinic)</td>
</tr>
</tbody>
</table>

Number of regimes corresponds to Table 1.
Fig. 4 shows a bright-field image from the surface layer of nickel implanted with titanium ions at regime Ni–Ti-II and the respective SAD pattern. The SAD pattern (Fig. 4b) is a series of individual diffraction rings. Analysis of the SAD pattern demonstrated that the implantation of titanium ions into nickel gives rise to formation of a surface layer consisting of compounds Ni₃Ti, NiTi₂ and TiNi as well as a solid solution of titanium in nickel. The highest intensity rings in the SAD pattern (Fig. 4b) correspond to reflections from the Ni₃Ti (004) and NiTi (020) phases. The ion-alloyed Ni layer, which is seen in the dark-field images in the respective reflections from the phases Ni₃Ti and NiTi, is a system consisting of a solid solution of titanium in nickel with inclusions of finely-dispersed intermetallic phases. According to the analysis of the dark-field images, the average grain size of the intermetallic phases (Ni₃Ti and TiAl) is equal to 40 nm for both regimes (Ni–Ti-I and Ni–Ti-II).

It has to be noted that apart from the above-mentioned intermetallic phases of Ti–Al, Ni–Al and Ni–Ti systems there was an observed formation of the titanium oxides (for Ti–Al, Ni–Ti systems) and aluminum oxides (for Ti–Al, Ni–Al systems) with different stoichiometric compositions and also titanium carbide (for Ti–Al system) (Table 2).

A comparison of the concentration profiles of implanted samples (Fig. 1) and the binary diagrams Ti–Al [10], Ni–Al [11] and Ni–Ti [12] allows us to identify the localization of phases formed under ion implantation. The regions of phase localization are presented in Table 2 and Fig. 1. The feature common to all systems is the structure of localization regions of the intermetallic phases and solid solutions of implanted metals.

Fig. 2. TEM images of the titanium surface layer implanted with aluminum ions in regime Ti–Al-I: (a) bright-field image, (b) SED pattern and (c) dark-field image.

Fig. 3. TEM images of the nickel surface layer implanted with aluminum ions in regime Ni–Al-II: (a) bright-field image, (b) SED pattern and (c) dark-field image.
in the targets. Three layers can be singled out, which are embedded into each other, with their thickness determined by the nature of the target. Layer 1 is the solid solution of implanted ions in a metal matrix, whose composition varies in depth and thickness coincides with that of the doped layer; layer 2 – contains the intermetallic compound \( \text{A}_3\text{B} = \text{Ti}_3\text{Al}, \text{Ni}_3\text{Al}, \text{Ni}_3\text{Ti} \); layer 3 – contains the intermetallic phase \( \text{AB} = \text{TiAl}, \text{NiAl}, \text{NiTi} \). Their thickness down from the irradiated surface decreases in the following order: layer 1 (solid solution) > layer 2 \( (\text{A}_3\text{B}) \) > layer 3 \( (\text{AB}) \).

3.3. Mechanical and tribological properties

Dependences of the microhardness on the indenter penetration depth for unimplanted materials (nickel and titanium) and ion-alloyed systems are presented in Figs. 5. The microhardness of all the implanted samples at depth to 2 \( \mu \text{m} \) is higher than that of the initial metals at the same depth. For example, the microhardness of the titanium sample implanted with regime Ti–Al-II increases by the factor of 1.5–3 in the surface region of ~1 \( \mu \text{m} \) thickness (Fig. 5).

We also investigated the tribological properties of implanted samples and the initial materials. Increase in temperature leads to a noticeable increase in the wear of the initial titanium and nickel materials. By contrast, wear of ion-alloyed samples is almost independent of the temperature. In particular, as the temperature increases to 473 K, the wear of initial titanium samples increases by a factor of 2.4 and of the initial nickel by a factor of 2, whereas wear of the ion-alloyed titanium sample remains virtually unchanged.

4. Conclusions

The high-intensity ion implantation provided by the Raduga-5 source makes it possible to produce implanted layers whose thicknesses are several orders larger than the ion projected range. It was found that an increase in the implantation dose leads to an increase in the implanted layer thickness up to 3 \( \mu \text{m} \). It has been shown that a higher ion dose under high-intensity ion-implantation treatment ensures that intermetallic layers as thick as a few microns can be formed and high concentration of the alloying impurity is archived.

Investigation of the ion-alloyed layers of nickel and titanium by the methods of TEM, RBS, and AES has shown that the surface layers of Ni and Ti targets are multi-phase systems containing nanosized intermetallic phases such as: \( \text{A}_3\text{B} \) and \( \text{AB} \) (\( \text{A}=\text{Ti}, \text{Ni}; \text{B}=\text{Al}, \text{Ti} \)) and solid solutions of implanted ions (Al or Ti) in these metals, with composition varying in depth. The increase in the implantation dose is accompanied by an increase in the size of grains of the formed phases in the ion-alloyed surface layers. A common characteristic feature has been revealed concerning the structure of localization of the intermetallic phases and solid solutions over the depth of ion-alloyed layers. Three regions could be singled out, each gradually changing into the other from the irradiated surface: three-phase
(A_B, AB and solid solution), two-phase (AB and solid solution) and one-phase (solid solution) regions.

The formation of ion-alloyed multi-phase layers containing intermetallic phases permits one to improve substantially the mechanical properties of materials. An important factor for practical applications is the possibility of forming ion-alloyed layers composed of several regions with different phase compositions. The formation of a mixture of intermetallic phases results in an extremely stable material resistant to corrosion and oxidation.

References