Research of mechanical properties of composite material based on titanium nickelide with a titanium surface layer depending on magnetron sputtering time

E O Nasakina¹, M A Sudarchikova¹, A M Tsareva¹, K V Sergiyenko¹, S V Konushkin¹, M A Kaplan¹, A S Baikin¹, L A Shatova² and M A Sevost'yanov¹

¹Baikov Institute of Metallurgy and Material Sciences, 49 Leninsky Avenue, Moscow, Russia;
²Voronezh State Technical University, st. 20-letiya Oktyabrya, 84/4, Voronezh, Russia.

Corresponding author’s e-mail: nacakina@mail.ru

Abstract. The regularities of the titanium surface and transitional monolayers formation using magnetron sputtering and ion bombardment depending on the deposition time, adhesion parameters and mechanical characteristics are investigated. Saturation regions of the surface and transition layers are noted. The transition layer provides high adhesion of the surface layer to the substrate. The application of a titanium surface layer to a nitinol reduces elongation and yield strength but increases tensile strength, and as the deposition time increases, the elongation decreases very slightly, and the yield strength and strength increase.

1. Introduction

In recent decades, composite materials have become more widespread and popular due to their much-increased capabilities compared to classical materials. The combination of several components in one object, forming a single, connected volume, and at the same time bearing each of their functional loads, allows not only to increase the characteristics of the future product but also to combine the properties of several traditional materials that were previously incompatible. Including layered composites, which are widely used in electronics, optics, medicine, in the creation of structural and other functional objects, can be effectively obtained using vacuum ion-plasma methods. One of such methods is magnetron sputtering, which contributes to the production of thin films and surface layers of a very different nature and thickness on the basis (substrates) of almost any composition and geometric configuration.

In this case, the parameters of the obtained layers are directly related to the process parameters, which can vary in a rather wide range: the time of sputtering, the relative position of the sputtered target from the material of the formed layer and the substrate onto which the layer is applied, in space, which determines the intensity of the resulting flow along with the power the process, the nature of the sprayed material and the condition of the surface on which it is applied, including determined by the phase composition of this surface. At the same time, the formation of new materials with a complex structure contributes to the multifunctionality of products made from them.

Nitinol exhibits biomechanical compatibility with living tissues, but also a controversial level of corrosion resistance and biocompatibility [1-16]. Titanium itself has high corrosion resistance and
ductility, biocompatibility and a coefficient of thermal expansion close to nitinol, therefore it can be effectively used as a surface layer in a layered composition with nitinol. Moreover, these properties, among other things, depending on the structure of the material, which depends on the formation parameters.

The purpose of the work was to study the mechanical properties of such a composition with different lengths of the surface layer.

2. Materials and methods
As a basis (substrate) of the formed composite materials used wire diameter of 280 μm samples of titanium nickelide composition of 55.91 wt. % Ni - 44.03 wt.% Ti (hereinafter TiNi) after sequential grinding of the surface with sandpaper with a grain size of 180 to 1000 grit and diamond paste (6-1 μm) to improve the surface quality. To clean, activate and polish the surface of the substrate, argon ions were bombarded with discharge parameters Ue = 900 V, Ie = 80 mA - preliminary ion etching. Chemically pure titanium was used as the surface layer material, which forms a single phase regardless of the process parameters, which facilitates the identification of the results.

The creation of metal composite materials was carried out by forming surface layers using a direct current magnetron (~ 865 mA) at a voltage of ~ 400 V in an argon gas medium at a working and residual pressure of ~ 0.4 and 4x10^-4 Pa, respectively, during the spraying time 5 -30 min at a spraying distance of 150 mm. The temperature on the surface of the substrates did not exceed 150 °C.

The morphology and layer-by-layer elemental composition (including using transverse sections) of the surface of the materials was studied using a TESCAN VEGA II SBU scanning electron microscope (SEM / SEM) equipped with an INCA Energy attachment for energy-dispersive analysis, and JEOL Auger electronic spectrometer JAMP-9500F combined with ion etching during argon bombardment at an angle of 30°. The X-ray diffraction spectra of the coating samples were recorded on an UltimaIV X-ray diffractometer (Rigaku, Japan) with a vertical goniometer and a high-speed D/teX semiconductor detector in CuKα radiation according to the Bragg – Brentano method and oblique shooting with a fixed angle turning the x-ray tube. Phase analysis of coating samples was performed in the PDXL software package using the ICDD database.

The mechanical properties of the studied samples were determined under conditions of static tension on a mechanical test machine INSTRON 3382, with a test speed of not more than 2 mm/min. The system complies with all European standards. Five samples were tested per experimental point. The yield strength, tensile strength and elongation were determined. Cyclic tests were conducted.

3. Results and discussion
Composite materials were obtained: “oxide layer (the region at the very boundary of the solid with the surrounding gas medium, free from substrate elements, where the titanium content is not at a maximum, about 20 nm thick) – the surface layer of the deposited substance – a transition layer containing elements of both a surface layer and basis – the basis” (Figure 1). The general pattern of changes in the composition of the composites obtained in this work is approximately the same in-depth.

With an increase in deposition time (Figure 2), the thickness of the surface and transition layers increases nonlinearly. Saturation regions of the surface and transition layers are noted, after which the thickness practically does not change with changing conditions.

Externally, the surface layer repeats the morphology of the substrate. Even with a short spraying time (5 min), uniform films are formed that do not differ from those obtained with a longer time. According to previous studies, at first, the formation of the layer has an island character, and then a more uniform distribution of the deposited substance on the surface occurs, while the atomized atoms (which acquire additional energy when sputtering from the target) are constantly mixed with surface atoms (substrates or previously deposited), which causes formation of a transition layer. It can be concluded that with a layer thickness of about 300 nm or more, the islands are smoothed in this work.
Figure 1. Layered composition surface morphology of a composite material with a titanium surface layer obtained in 30 min at a distance of 150 mm, a current of 865 mA and a voltage of 400 V, and a wire base made of nitinol.

X-ray diffraction patterns of samples with a titanium layer (Figure 3) show that the phase composition of the substrate does not change depending on the duration of the deposition of the layer. Regardless of the thickness of the layer, its phase composition also remains unchanged and is represented by beta-titanium, and does not correspond to the phase composition of the cast sputtering target.

Figure 4 shows a view of fractures of wire samples. It was noted that the layers had very high adhesion to the substrate and each other, breaking down as a single material and not peeling off except for the fracture zone. The destruction of all samples occurred almost identically. The fracture surface was oriented perpendicular to the tensile axis, representing a set of different-sized pores of a viscous fracture. Preliminary ion etching promotes better adhesion by promoting the formation of a uniform transition layer between the substrate and the deposited surface layer.

The results of the study of the mechanical properties of the composites are shown in Table 1. The application of a titanium surface layer to a titanium nickelide wire decreases the elongation and yield strength but increases the tensile strength, and as the deposition time increases, the elongation decreases very slightly, and the yield and strength limits increase.

According to the results of cyclic tests (Figure 5), we can conclude that delay and superelasticity are manifested in all samples. However, when applying a metal surface layer to a TiNi wire by magnetron sputtering, the flow stress decreases. Presumably, this occurs as a result of local heating of the surface layer and structural changes in the surface layers, including an increase in the initial fraction of martensite, which leads to a transition at lower loads. Also, the relaxation of residual stresses on the surface of the sample can occur.
Figure 2. Dependence of the thicknesses of the surface and transition layers of a composite obtained in 30 min at a current of 865 mA and a voltage of 400 V, depending on the spraying distance.

Figure 3. Composite material with a surface layer of titanium, obtained at a distance of 150 mm for 30 minutes.
Figure 4. SEM image of composite wires with a titanium (a) and tantalum (b) surface layers obtained in 30 min at a distance of 150 mm, a current of 865 mA and a voltage of 400 V, on a wire base of nitinol.

Table 1. Mechanical characteristics of a nitinol substrate and a composite with a titanium surface layer.

| Sample          | Elongation, % | Yield Strength (MPa) | Tensile strength (MPa) |
|-----------------|---------------|----------------------|------------------------|
| As-received TiNi| 7.57          | 661                  | 1240                   |
| Polished TiNi   | 7.99          | 706                  | 1242                   |
| Ti@NiTi 5 min.  | 6.64          | 447.00               | 1154.00                |
| Ti@NiTi 10 min. | 6.43          | 460.33               | 1452.00                |
| Ti@NiTi 20 min. | 6.29          | 480.00               | 1461.50                |
| Ti@NiTi 30 min. | 6.24          | 520.33               | 1475.6                 |
4. Conclusions

The regularities of the formation of surface and transitional monolayers of titanium using magnetron sputtering and ion bombardment depending on the time of deposition are investigated, and adhesion parameters and mechanical characteristics of all the materials obtained are determined.

The metal composite materials had the structure “oxide layer – the surface layer of the deposited substance – a transition layer containing elements of both a surface layer and basis – the basis”. The surface morphology corresponds to the surface morphology of the substrate.

As the sputtering time increases, the thickness of the metal surface layer increases nonlinearly. Saturation regions of the surface and transition layers are noted, after which the thickness practically does not change with changing conditions. The transition layer provides high adhesion of the surface layer to the substrate.

The application of a titanium surface layer to a titanium nickelide wire reduces elongation and yield strength but increases tensile strength, and as the deposition time increases, the elongation decreases very slightly, and the yield strength and strength increase.

Figure 5. The results of cyclic mechanical tests for a) nitinol and b) a composite obtained in 30 minutes.
Acknowledgments
This work was supported by the Russian Foundation for Basic Research under project No. 19-08-00642 A.

References
[1] Davis J R. 2003 Handbook of materials for medical devices (ASM Int.) 350 p
[2] Nasakina E O, Sudarchikova M A, Sergienko K V, Konushkin S V, Sevost’yanov M A 2019 Ion Release and Surface Characterization of Nanostructured Nitinol during Long-Term Testing Nanomaterials 9(11) 1569
[3] Petreni L, Migliavacca F 2011 Biomedical Applications of Shape Memory Alloys Journal of Metallurgy 2011 1-15
[4] Duerig T W, Melton K N, Wayman C M, Stockel D 1990 Engineering aspects of shape-memory alloys (Oxford: Butterworth Heinemann Ltd) pp 181 – 194
[5] Shabalovskaya S 1996 On the nature of the biocompatibility and medical applications of NiTi shape memory and superelastic alloys Bio Med Mater Eng 6 267 – 289
[6] Marjan Bahrami Nasab, Mohd Roshdi Hassan 2010 Metallic Biomaterials of Knee and Hip - A Review Trends in Biomaterials and Artificial Organs 24(1) 69 - 82
[7] Surdell D, Shaibani A, Bendok B, Eskandari M K 2007 Fracture of a Nitinol Carotid Artery Stent That Caused Restenosis J Vasc Interv Radiol 18(10) 1297–1299
[8] Bose A, Hartmann M, Henkes H A 2007 Novel, Self–Expanding Nitinol Stent in Medically Refractory Intracranial Atherosclerotic Stenosis: Wingspan Study Stroke 38 1531–1537
[9] Stoeckel D, Pelton A, Duerig T 2004 Self-expanding nitinol stents: material and design considerations Eur Radiol 14 292-301
[10] Xiaoying Lu, Xiang Bao, Yan Huang, Yinghua Qu, Huiqin Lu, Zuhong Lu 2009 Mechanisms of cytotoxicity of nickel ions based on gene expression profiles Biomater 30 141–148
[11] Uo M, Watari F, Yokoyama A, Matsuno H, Kawasaki T 1999 Dissolution of nickel and tissue response observed by X-ray scanning analytical microscopy Biomater 20 747–755
[12] Wataha J, O’Dell N, Singh B, Ghazi M, Whitford G, Lockwood P 2001 Relating nickel-induced tissue inflammation to Ni release in vivo J. Biomed. Mater. Res. 58 537–544
[13] Balazic M, Kopac J 2007 Improvements of medical implants based on modern materials and new technologies J. Achiev. Mater. Manuf. Eng 25(2) 31-34
[14] Kim J H, Shin J H, Shin D H, Moon M W, Park K, Kim T H et al. 2011 Comparison of diamondlike carbon-coated nitinol stents with or without polyethylene glycol grafting and uncoated nitinol stents in a canine iliac artery mode Br J Radiol 84 210-215
[15] Tomić S, Rudolf R, Brunčko M, Anžel I, Savić V, Čolić M 2012 Response of monocyte-derived dendritic cells to rapidly solidified nickel-titanium ribbons with shape memory properties Eur. Cell. Mater. 23 58–81
[16] Chun-Che Shih, Shing-Jong Lin, Yuh-Lien Chen, Yea-Yang Su, Shiau-Ting Lai, Gaston J. Wu, Ching-Fai Kwok, Kwok-Hung Chung. 2000 The cytotoxicity of corrosion products of nitinol stent wire on cultured smooth muscle cells J. Biomed. Mater. Res. 52 395–403