Production of niobium vacuum-arc coating on a TiNi-based alloy

K. S. Senkevich[†,1], D. E. Gusev[1], N. N. Sitnikov[2], E. A. Vysotina[2],

O. Z. Pozhoga[1], S. M. Sarychev[1]

[1]Moscow Aviation Institute (National Research University), 4 Volokolamskoe shosse, Moscow, 125993, Russia
[2]Federal State Unitary Enterprise Keldysh Research Center, 8, Onezhskaya St., Moscow, 125438, Russia

†senkevichks@yandex.ru

The aim of this work is to produce a niobium coating by vacuum-arc deposition on a TiNi-based alloy. This method has not been studied in relation to titanium nickelide base alloys and is promising for the production of corrosion and wear resistant coatings for medical and technical applications. The niobium coating is deposited on the semi-finished products (wire and cylindrical specimens) made of titanium nickelide base alloy of composition $Ti_{49.4}Ni_{50.6}$ (at pct) and the surface subjected to mechanical grinding. It is stated that the obtained coating with a thickness of about 1 μm possesses drawbacks, such as 'inherited' surface profile formed by mechanical grinding of semi-finished products, and the drop phase, which is a typical unavoidable defect for this type of deposition method. At the same time, the surface layer of the alloy with a niobium coating exhibits a significantly higher microhardness (two times more) than the initial alloy. The effect of the revealed defects on the corrosion properties and wear resistance of the alloy requires further study. Bending deformation is used to study the mechanical behavior of the wire in the initial state and after coating deposition; it is stated that the coated wire exhibits superelastic behavior in bending identical to the initial wire. At the same time, deposition of the coating causes the formation of internal stress fields near the wire surface, and the effects of these fields lead to the elimination of non-recoverable deformation in the unloaded wire accumulated in the subsurface layers under loading.

Keywords: niobium coating, shape memory alloy, vacuum-arc deposition.

Получение вакуумно-дугового покрытия из ниобия на сплаве на основе TiNi

Сенкевич К. С.[†,1], Гусев Д. Е.[1], Ситников Н. Н.[2], Высотина Е. А.[2],

Пожога О. З.[1], Сарычев С. М.[1]

[1]Московский авиационный институт (Национальный исследовательский университет),
Волоколамское шоссе, 4, Москва, 125993, Россия
[2]ГНЦ ФГУП «Центр Келдыша», ул. Онежская, 8, Москва, 125438, Россия

Целью настоящей работы является получение покрытия из ниобия методом вакуумно-дугового напыления на сплаве на основе TiNi (никелид титана, нитинол). Этот метод не исследован применительно к сплавам на основе никелида титана, и перспективен для получения коррозионно и износостойких покрытий для медицинских и технических применений. Покрытие из ниобия наносили на полуфабрикаты (проволоку и цилиндрические образцы) из сплава на основе никелида титана составом $Ti_{49.4}Ni_{50.6}$, имеющую поверхность, сформированную при механическом шлифовании. Установлено, что полученное покрытие толщиной около 1 мкм обладает недостатками в виде "наследственного" поверхностного рельефа, сформированного при механической шлифовке полуфабрикатов сплава, а также типичным неизбежным дефектом, присущими данному методу напыления покрытий — капельной фазой. При этом поверхностный слой сплава с ниобиевым покрытием обладает значительно более высокой микротвёрдостью (более чем в два раза), чем исходный сплав. Роль данных дефектов на коррозионные свойства и износостойкость сплава требуется дополнительно изучить. Методом деформации при изгибе изучено механическое поведение проволоки из сплава в исходном состоянии и с покрытием, и установлено, что проволока с покрытием

показывают аналогичное сверхупругое поведение при изгибе как и проволока в исходном состоянии. При этом нанесение покрытия вызывает формирование вблизи поверхности проволоки внутренних полей напряжений, действие которых приводит при разгружении проволоки к устранению невосстановленной деформации, которая была накоплена в приповерхностных слоях при их нагружении.

Ключевые слова: покрытие из ниобия, сплав с памятью формы, вакуумно-дуговое напыление.

1. Introduction

TiNi-based alloys are promising materials for the production of medical implants due to their unique superelastic behavior being similar to the elastic behavior of human bone tissues [1, 2]. One of the main reasons to restrain more active application in medicine is the presence in the alloy of carcinogenic nickel, which is toxic to the human body. Despite different investigations on the biological compatibility and corrosion resistance of titanium nickelide, which have shown an improbable toxic reaction to the human body [3 – 5], various methods of improving bioinactivity are being studied. To solve this problem, different modes of modifying the surface of the alloys [6 – 10] or coating deposition of elements with a higher biological compatibility and corrosion and wear resistance [11 – 15] are considered. The best known are the cases of improving the corrosion resistance of titanium nickelide base alloys by means of biocompatible tantalum, silicon, zirconium, and titanium coatings [9,11 – 14,16,17] produced by magnetron deposition and ion sputtering or ion implantation.

An advanced method to improve the corrosion resistance of biomaterials is the deposition of a biocompatible niobium coating. The reports [18,19] show that the niobium barrier coating improves the corrosion resistance of dental implants made of stainless steel. Investigations on the effect of the niobium coating on the corrosion resistance of titanium nickelide base alloys have not been conducted; however it is known that even alloying with niobium or creation of Ti-Ni-Nb surface films improve their corrosion resistance [20, 21]. The report [22] shows that the niobium coating on Ti-50.8 Ni at pct alloy has good adhesion strength.

The aim of the work is to produce a niobium coating on TiNi-based alloy by vacuum-arc deposition. This method is scarcely studied concerning titanium nickelide base alloys and is promising for the creation of corrosion and wear resistant coatings for medical and technical application.

2. Experimental Methods

The niobium coating was deposited on a wire with a diameter of 2.2 mm and cylindrical specimens with a diameter of 14 mm, made of titanium nickelide base alloy with the composition of $Ti_{49.4}Ni_{50.6}$ (at pct), and the surface subjected to mechanical grinding. Industrial alloy is obtained by induction smelting, and after performing standard operations of forming an ingot, the bulk structure of the alloy is presented by the B2 phase matrix and inclusions of Ti_2Ni intermetallic phase particles, the amount of which is about 7% of the volume fraction of the alloy (Fig. 1b). The wire of the alloy is in the superelastic austenitic state since it has the following martensitic transformation (MT) temperatures: $M_s = -45°C$, $M_f = -60°C$, $A_s = -30°C$, $A_f = -12°C$.

The niobium coating was deposited in an argon medium using vacuum-arc deposition (cathode arc deposition) through the substrate plating with the material out of the plasma flows generated in a cathode spot of vacuum arc of high-current and low-voltage low-pressure discharge, which develops exclusively in vapor of sputtered cathode materials. This method is also called arc ion plating (AIP). Before the deposition process, ion cleaning of the semi-finished products had been carried out in order to remove contamination and scale residue. The deposition was carried out at an argon pressure in the chamber of $P = 9 \cdot 10^{-3}$ mm Hg. The temperature was 400°C. The time of the process was as follows: 20 minutes for ion cleaning, and 30 minutes for coating deposition.

The surfaces of the coated and uncoated wire were studied using a JSM-6060A (JEOL) scanning electron microscope. To study the influence of the deposited coating on the functional properties of the alloy, the wire was subjected to a three-point bending test (the distance between the lower bearings of the test facility equaled 25 mm) using a TIRAtest 2300 machine at normal temperature. The stress analysis of the wire was carried out according to the formula $\sigma = M / W$ (M is the bending moment and W is the modulus of the section). Microhardness was measured using a MicroMet 5101 device using a diamond pyramid with a load of 0.5 N. The surface roughness was measured using a «HOMMEL TESTER T500» device, and the surface roughness parameters were determined as follows: average roughness R_a and profile depth R_{max}.

3. Experimental Results and Discussion

Electron microscopic analysis of the wire surface in the initial state showed that it had a profile with parallel grooves formed during mechanical grinding (Fig. 1a). This type of profile can impair corrosion behavior of TiNi-based alloys. Fig. 1c, d show outer view of the surface and surface layer view of the wire after the niobium coating deposition has been applied. Typical features of the AIP method can be observed on the surface of the wire, such as traces of the drop phase in the form of protuberances and craters, which is a drawback of this method and can affect the corrosion resistance of the alloy. In addition, the coating deposition has a slightly smoothed microprofile of the surface of the wire and linear grooves are still observed after mechanical grinding. Measurement of roughness in semi-finished products showed its increase after coating deposition. Thus, in the initial state R_a and R_{max} parameters of the wire equaled 0.2 and 2.14 µm, respectively, and for a cylindrical specimen are 0.09 and 1.34 µm, respectively. After coating deposition, the surface roughness parameters (R_a and R_{max}) of the wire are 0.47 and 3.32 µm, respectively, and for a cylindrical specimen are 0.11 and 1.47 µm, respectively. This increase in

roughness is associated with the presence of a drop phase on the coating surface, which is typical for the coatings obtained by the vacuum-arc method [23].

Analysis of the structure of the surface layer in the semi-finished products from the alloy showed that the applied mode of vacuum-arc deposition made it possible to form a niobium coating with a thickness of about 1 μm. The results of X-ray spectrum microanalysis (Fig. 2) show that the surface layer consists mainly of niobium (97.44 wt. pct), and also contains a small amount of basic elements — titanium (0.37 wt. pct), nickel (1.92 wt. pct), and iron as a technological impurity (0.28 wt. pct).

A comparative analysis of microhardness for cylindrical specimens of the alloy in the initial state and after coating deposition showed that the niobium-containing surface layer (penetration depth of the indenter 1.9 μm) exhibited significantly higher values of hardness than the surface layer of the initial alloy — 1100 ± 46 and 450 ± 25 HV, respectively. The same sharp increase in the hardness of the surface layer is typical for titanium nickelide base alloys coated with molybdenum and tantalum [24].

Changes in the structural state of the surface layers should have an impact on the mechanical behavior of the alloy [24], especially when maximum strains occur on the surface of the wire, for instance during bending. A three-point bending test of an uncoated wire showed that the alloy exhibited good superelastic properties at normal temperature. The mechanical behavior of the alloy is defined by a typical flag-shaped deformation curve with a strongly pronounced stress hysteresis ($250 \div 350$ MPa), observed between the loading and unloading curves (Fig. 3). Such a mechanical behavior is typical for TiNi-based alloys in the superelastic
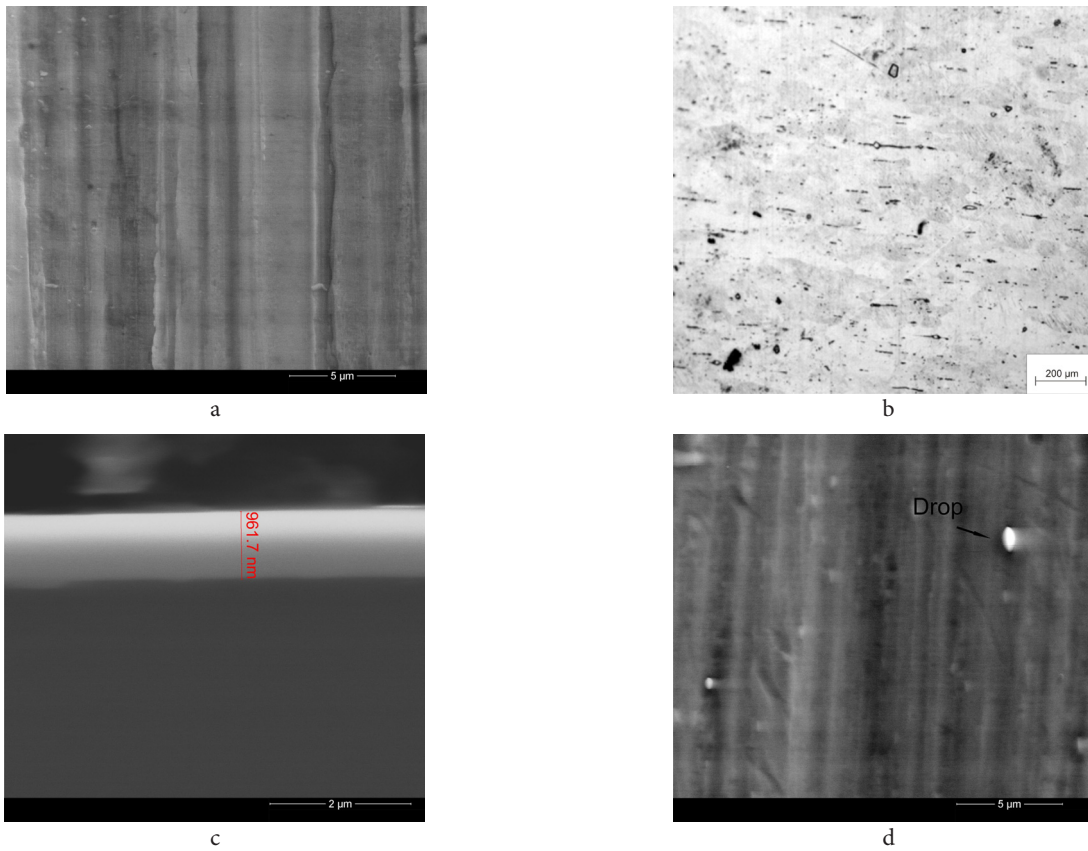
Fig. 1. Structure of the TiNi-based alloy: surface view (a) and bulk structure (b) of the wire in the initial state, surface layer cross-section (c) and surface view in the niobium coated wire (d).
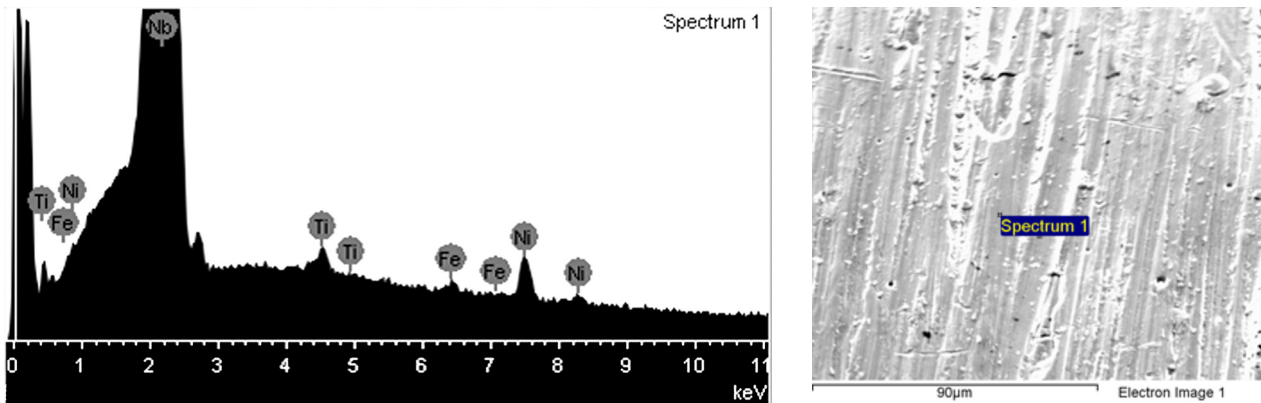
Fig. 2. Results of the X-ray spectrum microanalysis (left) for the surface layer of the niobium coated wire (right).

austenitic state at martensitic transformation temperatures below 0°C.

When the deformation degree exceeds its critical value [25], equaled about 4.5%, sliding begins to develop in the alloy, which results in the accumulation of non-recoverable strain in the wire. Cyclic loading of the wire for 5 cycles with a maximum deformation of 5% has a slight effect on the superelastic behavior of the alloy, but the strain level of the martensitic shear decreases to some extent ($\sim 80 \div 100$ MPa).

The coated wire exhibits in general a similar superelastic behavior under bending when loading and unloading deformation curves are practically identical to the same curves obtained for the uncoated wire. At the same time, it can be noted that the stresses under which direct and reverse martensitic transformations occur in the coated wire are approximately $50 \div 100$ MPa lower than that for the uncoated wire. Since the maximum strains occur on the surface of the wire under bending, it can be assumed that the decrease in the level of martensitic shear stresses is conditioned by structural changes in the surface under coating deposition. Another cause for the decrease in martensitic shear stresses may be a slight increase in the temperature of the martensitic transformation in the alloy caused by thermal holding during coating deposition. It is known [26, 27] that heating and long-term holding (at least one hour) at temperatures of about 400°C can result in structural changes connected with the precipitation of nickel-enriched intermetallic particles, as well as in an increase in the MT temperatures. However, short-term holding for 30 min cannot substantially change the MT temperatures and the superelastic behavior of the alloy, which is observed in Fig. 3 b. This low-temperature effect also cannot result in a change in the volume fraction of the Ti_2Ni particles and a respective change of titanium-to-nickel percentage ratio in the matrix of the alloy, since these particles are thermally stable up to high temperatures [28].

In addition, a change in the structural state in the surface layers results in removal of plastic deformation accumulated by sliding at the final stage of unloading for the coated wire after exceeding the critical deformation during bending tests. This is a distinctive feature of the mechanical behavior of coated wire as opposed to that of the uncoated wire. It should be noted that in case of loading and following unloading of uncoated wire parts of the deformation curves corresponding to the elastic behavior of the material coincide with each other when the non-recoverable deformation is not observed, and under the non-recoverable deformation these parts are parallel. However, under cyclic loading the inclination angle of the elastic part in the unloading curve gradually decreases due to internal strains arising in the subsurface layers of the wire, which are caused by the accumulation of lattice defects in the alloy. The coated wire exhibits a totally different behavior. When the deformation exceeds its critical value (4.5%), the inclination angle of the elastic part on the deformation curve under unloading is always less than that on the curve under loading, and non-recoverable deformation is not observed. This evidences that the coating deposition causes the formation of internal stress fields nearby the wire surfaces, and the effects of these fields result in the removal of non-recoverable deformation accumulated in the subsurface layers of the wire under bending.
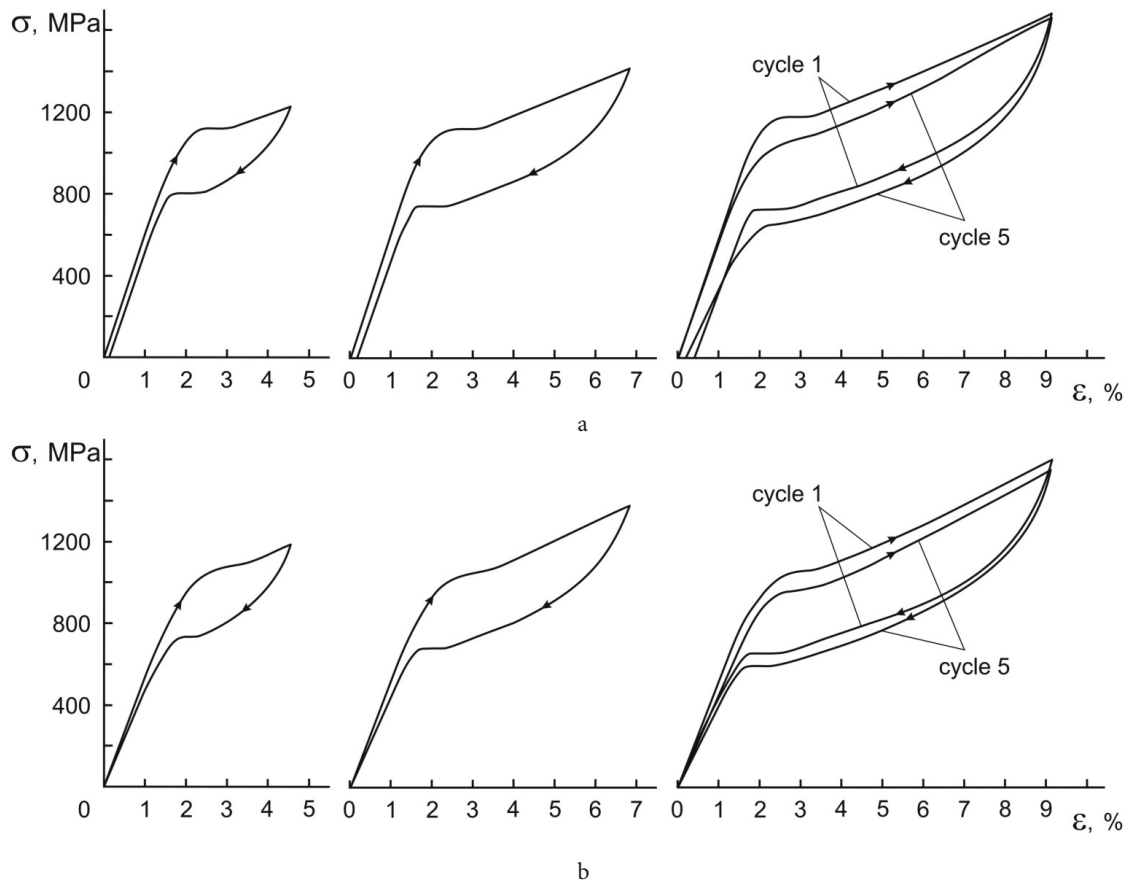

Fig. 3. Bending deformation curves: uncoated wire (a), wire with coating (b).

Conclusions

1. The vacuum-arc deposition method has been applied for the first time to a titanium nickelide base alloy to produce a niobium coating with a thickness of about 1 μm and high microhardness. It is stated that the coating possesses drawbacks, such as the 'inherited' surface profile formed during mechanical grinding, as well as the drop phase being unavoidable defect typical for this method of coating deposition. The role of these defects in the corrosion properties and wear resistance of the alloy requires further study.

2. The method of bending deformation is used to study the mechanical behavior of the alloy in the initial state and after coating deposition. It is stated that the coated wire exhibits similar elastic behavior under bending as the uncoated wire. At the same time, the coating deposition causes the formation of internal stress fields near the wire surfaces, and when the wire is unloaded, the effects of these fields result in the removal of non-recoverable deformation accumulated in the subsurface layers of the wire under loading.

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