UDC: 538.971: 621.039.64

MODIFICATION OF TiN COATINGS BY ELECTRON IRRADIATION

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This work presents the experimental results of structural and phase changes research study in TiN coatings under thermal and electron irradiation. Continuous electron irradiation of coated samples was performed on the ELV-4 accelerator. It was determined that electron irradiation with an electron energy of 1.3 MeV and an integral irradiation dose of $0.52\cdot10^{19}$ e^{-}/cm^{2} leads to an increase in the microhardness of TiN coatings by 20%. It has been established that the main factor in increasing the microhardness of the coating after electron irradiation in the above regimes is the formation of new phases, in particular the intermetallide of Co_2Ti.

Keywords: coating, hardness, electron irradiation, titanium nitride, structure.

INTRODUCTION

Recently, we have been carried out the intensive research of the structural-phase state and functional properties relationship of nitride coatings, depending on the methods and conditions of their synthesis [1–3]. As the main direction of development of plasma coating methods in vacuum, a decrease in defects and porosity of coatings, an increase in their adhesive strength, the formation of multilayer coatings, the formation of coatings with improved performance characteristics and high hardness can be noted. To solve these problems, combined processing technologies are used, including ion-plasma coating and subsequent surface treatment with thermal, laser, ion-plasma and electron beam effects. Such treatments make it possible to optimize the physic mechanical properties of the applied coatings [4, 5]. Thus, reducing the porosity of a plasma cermets coating while increasing the strength of its bond with the substrate is possible by heat treatment of the coating. To implement in practice the high-temperature treatment of the coating without heating the sprayed substrate is possible with laser, ionic or electron irradiation of the coating [6]. In this regard, in this paper, the task is to study the peculiarities of the modification of the protective coating of TiN using electron-beam processing and to establish the effect of electron irradiation on the structure and microhardness of the protective coating of TiN.

1. MATERIALS AND METHODS OF RESEARCH

TiN-based coatings were obtained at the «Bulat-6» installation using vacuum arc deposition at LLP «Mashzavod», Ust-Kamenogorsk, Kazakhstan. To carry out vacuum arc deposition, flat samples were made with dimensions of [20×20×0.5] mm, after preliminary thermo mechanical treatment: quenching from 950 °C (10 min) and rolling by 90%. The sputtering of a metal target was carried out in a mixture of the working gas $Ar+N_2$. The substrate temperature during spraying did not exceed 2000°C. Austenitic hardening alloy 67CoNi5Nb (67% – Co, 28% – Ni, 5% – Nb) was chosen as the substrate.

The principle of the Bulat-6 installation work is concluded in followings: the substrate is prepared and fixed in the tooling; a vacuum is created in the chamber, then an electric drive is switched on, transmitting the planetary rotation around its axis to the parts, the substrate also rotates around the cathode; after driving the part and the cathode, which goes back and forth along the main axis, turn on the anode coils; then the electromagnetic lock is actuated and the electric displacement potential is applied with a negative index to the substrate, thus a vacuum arc discharge is initiated between the cathode and the anode. Discharge burning supports the inverter power supply. The target turns into plasma that covers the detail.

Sustained electron irradiation of coated samples was carried out at the ELV-4 accelerator at JSC «Park of Nuclear Technologies», Kurchatov, Kazakhstan. The electron energy on the surface of the samples during irradiation was 1.3 MeV, and the beam current density was 10 $\mu A\cdot cm^{2}$. Samples were irradiated at doses of $0,08\cdot10^{19}$ e^{-}/cm^{2} and $0,52\cdot10^{19}$ e^{-}/cm^{2}.

The electron accelerator ELV-4 was installed and put into operation at Institute of Nuclear Physics of the National Nuclear Center of the Republic of Kazakhstan as a basic installation for the adaptation and development of electron-beam technologies in the Republic of Kazakhstan. Direct-acting electron accelerator, based on an induction cascade multiplier. Acceleration of electrons is provided by a metal-ceramic accelerator tube. The electron source is a lanthanum hex boride cathode with indirect heating. The beam of accelerated electrons from the vacuum chamber is brought into the atmosphere through a titanium foil 100 microns thick. The scan of the beam on the foil is a scanning device in two mutually perpendicular directions. The evacuation of the accelerator tube to the vacuum and the beam extraction system is provided by magnetic discharge pumps. The installation allows you to accelerate electrons with energy up to 1.5 MeV at a maximum beam power of up to 40 kW. The accelerator is used to solve scientific and applied problems, in particular,

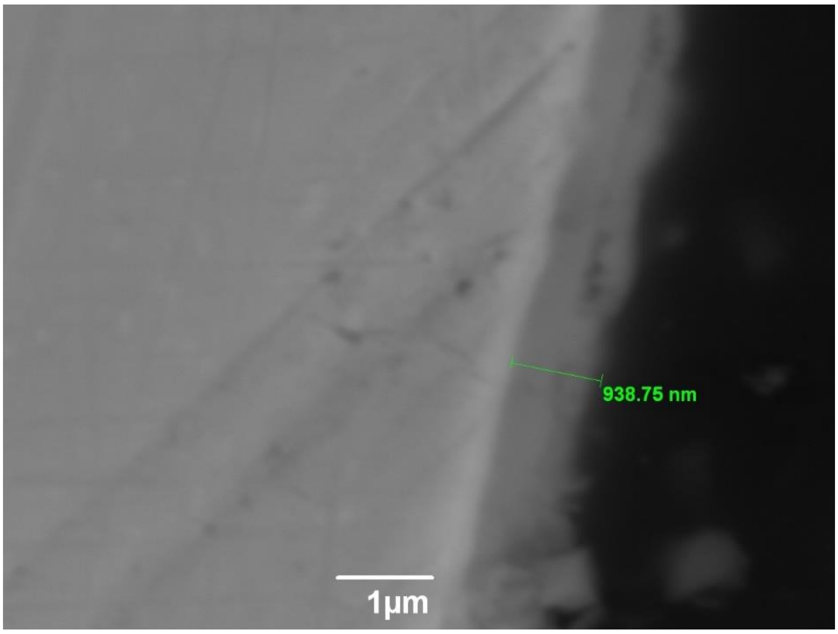

Fig 1. SEM-image of the cross section of the TiN coating

for radiation cross linking of polymers and radiation processing of medical products.

The research of the phase composition and crystal structure of alloy samples was carried out by X-ray diffraction analysis on an X'Pert Pro diffractometer in CuKα-radiation. The morphology and composition of the surface of the samples was studied on a JSM-6390LV scanning electron microscope equipped with an energy dispersive analysis attachment. Microhardness measurements were carried out on the device PMT-3 in accordance with GOST 9450-76.

2. The results of research and discussion

The influence of different modes of electron-beam processing on the morphology of the formed surface and the elemental composition of the coatings was studied in the process of research. Figure 1 shows a cross-sectional image of a coated sample. It is seen that the formed coatings are characterized by a dense, faceless structure, without visible pores and cracks caused during deposition. Coating thickness is about 1 μ. It can be seen from the figure that there are three areas: the precipitation layer, the diffusion layer, and the matrix.

The Vickers microhardness histograms for synthesized coatings under loads of 100 and 150 g are shown in Figure 2. It is clear that the hardness value under loads of 100 g is higher than with a load of 150 g, which, due to the small thickness of the coating, exceeds the depth of extrusion of the coating with a load of 150 g. The most reliable results will be obtained with a load of 100 g. The hardness of the initial coatings is Hμ≈11 G Pa. After irradiation to a dose of $0.52 \cdot 10^{19}$ e^{-}/cm^2, the microhardness of TiN coatings increases by 20% compared with the initial value, which is consistent with the idea of the strengthening effect of electron beam treatment on coatings [7]. In order to establish the main factors affecting the increase in hardness, we studied the phase states of coatings before and after irradiation.

A qualitative phase analysis of the coatings deposited on the 67CoNi5Nb alloy was performed. Figure 3 shows the diffraction pattern of the substrate (Fig. 3, a) and the substrate with a coating of TiN before (Fig. 3, b) and after electron irradiation (Fig. 3, c–d). It is seen that the main phase of the substrate is Co. X-ray data show that the initial coating consists of phases TiN and Co_2N. The results obtained indicate that during the deposition of coatings, nitrogen interacts with the alloy (substrate), which leads to the formation of the Co_2N phase. Due to the small thickness of the coating, the reflections of the Co_2N phase can be clearly seen from the diffractogram. Thus, the calculated depth of penetration of the x-ray beam for the TiN phases is about 10–15 μm (when the angle 2θ is changed from 30 to 80°).

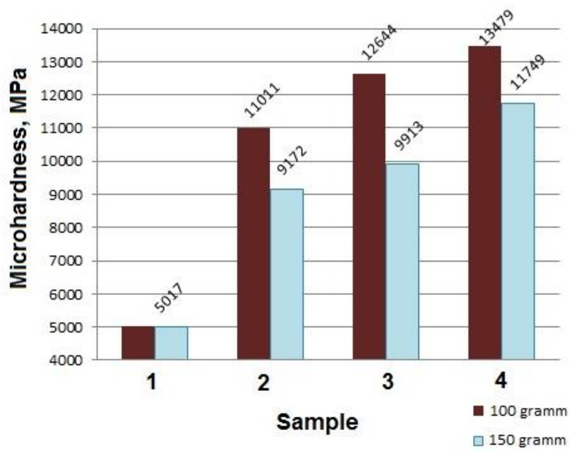

Fig. 2. Microhardness histogram depending on the processing and load on the indenter 100 g and 150 g

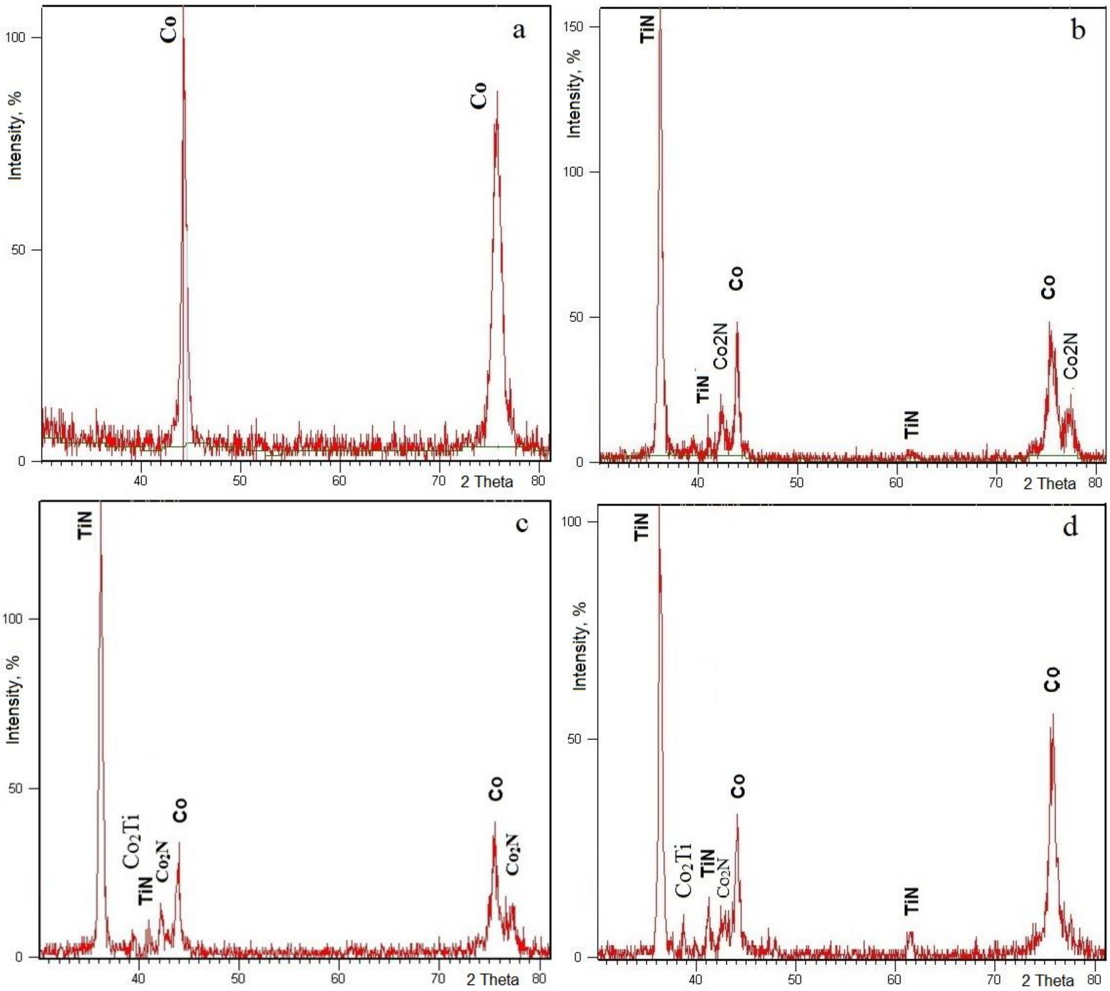

Fig 3. Diffractograms of an alloy 67KN5B (a) with TiN-coated before (b) and after irradiation with electrons to a dose of $0.08\cdot10^{19}$ e^{-}/cm^2 (c) and $0.52\cdot10^{19}$ e^{-}/cm^2 (d)

The formation of Co_2Ti intermetalide is observed after electron irradiation. With an increase in the radiation dose to $0.52\cdot10^{19}$ e^{-}/cm^2, an increase in the intensity of the Co phase is observed. All this is explained by the redistribution of the elements of the substrate and the coating during the irradiation with an electron beam.

Thus, it can be argued that the main factor in increasing the microhardness of the coating after irradiation is the formation of new phases, in particular, the Co_2Ti intermetallide (Laves phase). Since, Laves phases are very hard and brittle compounds [8]. Also, it is assumed that the ongoing phase formation and redistribution of alloying elements lead to an improvement in adhesion between the base material and the coating.

Figure 4, a–c shows the SEM-images of the surface of the coatings before and after electron irradiation. Electron microscopic studies showed that TiN coatings have craters and fine particles. After electron irradiation, no significant changes in the surface morphology were found. To determine the chemical composition of micro-defects and precipitates, a microanalysis was performed in the energy dispersive analysis mode (Fig. 5, a–c).

Table. The chemical composition of the surface of the alloy with TiN-coatings

Mode of Profes-sion	Spec-trum	N	Ti	Fe	Co	Ni	Nb	Total, %
Initial	1	37.65	61.75		0.60			100.00
	2	27.70	71.30		0.99			100.00
	3	35.66	63.64		0.71			100.00
	4		58.34	1.01	38.69	1.96		100.00
	5	27.31	71.69		1.00			100.00
	6	29.49	69.54		0.97			100.00
After irradiation with a dose of $0.08\cdot10^{19}$ e^{-}/cm^2	1	23.86	73.22		1.89	1.03		100.00
	2	27.35	67.82		3.29	1.54		100.00
	3	28.47	36.54	0.66	23.41	9.52	1.40	100.00
After irradiation with a dose of $0.52\cdot10^{19}$ e^{-}/cm^2	1	28.50	70.78		0.72			100.00
	2	35.09	64.25		0.66			100.00
	3	28.88	68.00		2.18	0.94		100.00
	4		33.32	1.19	42.93	19.39	3.17	100.00

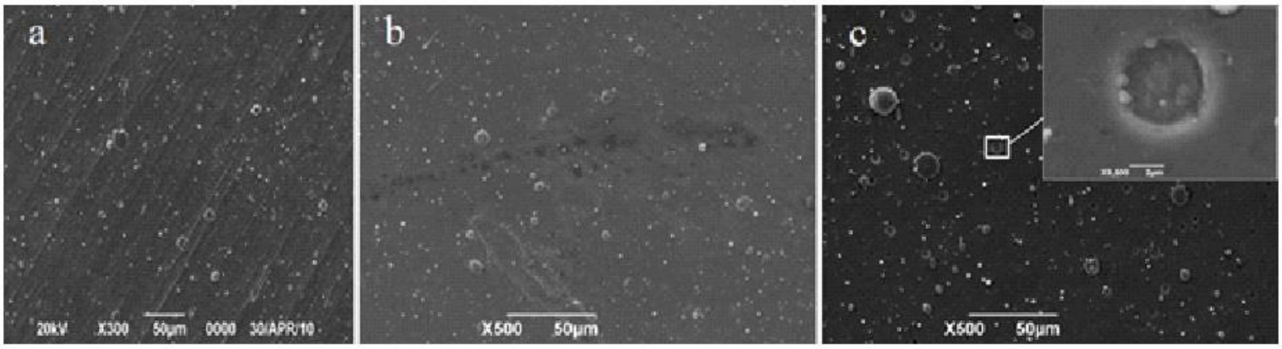

Fig. 4. Microstructures of the surface of TiN-coatings before (a) and after electron irradiation with a dose of $0.08{\cdot}10^{19}$ e⁻/cm² (b) and $0.52{\cdot}10^{19}$ e⁻/cm² (b)

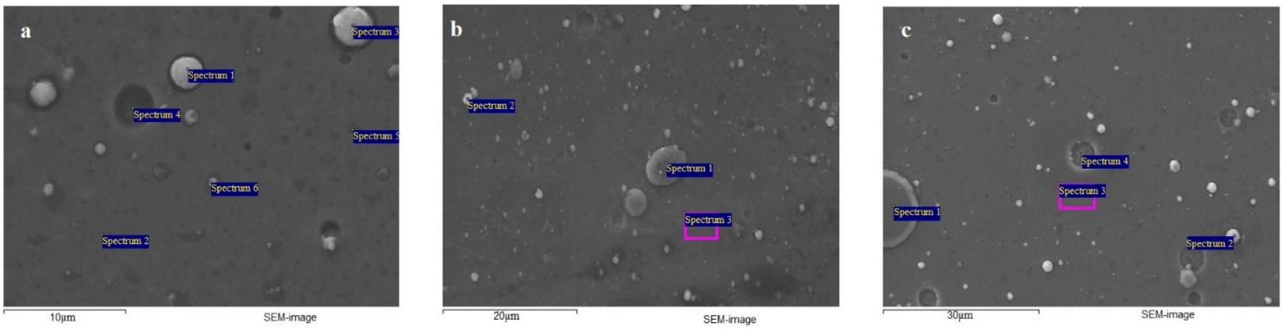

Fig. 5. SEM-images of the surface of the TiN-coating before (a) and after annealing (b), electron irradiation with a dose of $0.08{\cdot}10^{19}$ e⁻/cм² (c) and $0.52{\cdot}10^{19}$ e⁻/cм² (g)

Figure 5 shows the areas selected for X-Ray analysis, but Table shows the chemical composition of the coating.

We can conclude that under the influence of electron irradiation a spatial redistribution of alloying elements of the alloy occurs from the analysis of the data in Table. At the same time, it was found that the amount of nickel formed in the composition of light droplet-shaped particles formed on the surface is larger compared to the composition of the base. Considering the wrap zone of energy dispersive analysis, which is much larger than the particle size, it is assumed that the light droplet-like particles are a phase based on Ni-Ti. The formation of these particles is associated with nickel segregation during electron beam irradiation. However, an X-ray analysis did not reveal any Ni-Ti-based phases, because of the low concentration of these phases.

CONCLUSION

Thus, the experimental research have shown that using electron irradiation with an electron energy of 1.3 MeV and an integral irradiation dose of $0.08{\cdot}10^{19}\div 0.52{\cdot}10^{19}$ e⁻/cm², it is possible to obtain modified solid protective coatings based on titanium nitride. It was determined that electron irradiation with an electron energy of 1.3 MeV and an integral irradiation dose of $0{,}52{\cdot}10^{19}$ e⁻/cm² leads to an increase in the micro-hardness of the TiN coating by 20%. It has been established that the main factor in increasing the microhardness of a coating after electron irradiation in the above regimes is the formation of new phases, in particular, Co_2Ti intermetallic.

Acknowledgements: *This work was supported by grant of the Committee of Science, Ministry of Education and Science of the Republic of Kazakhstan.*

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ЭЛЕКТРОНДЫҚ СӘУЛЕЛЕНУ КЕЗІНДЕГІ ТИТАН НИТРИДІ ЖАБЫНДАРЫНЫҢ МОДИФИКАЦИЯСЫ

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Аталған жұмыста термиялық және электрондық сәулелену кезіндегі титан нитриді (TiN) жабындарының құрылымдық және фазалық өзгерістерін зерттеудің эксперименттік нәтижелері берілген. Жабындық үлгілерді үздіксіз электрондық сәулелендіру ЭЛВ-4 үдеткішінде жүргізілді. 1,3 МэВ электрондар энергиясымен және $0.52 \cdot 10^{19}$ е⁻/см² интегралды сәулелену дозасымен электрондық сәулелендіру TiN жабындары микроқаттылығының 20%-ға артуына әкелетіні анықталды. Жоғарыда көрсетілген режимдерде электрондық сәулеленуден кейін жабынның микроқаттылығын арттырудың негізгі факторы жаңа фазалардың, атап айтқанда Co_2Ti интерметаллидінің пайда болуы болып табылатындығы анықталды.

Кілт сөздер: жабын, қаттылық, электрондық сәулелену, титан нитриді, құрылым.

МОДИФИКАЦИЯ НИТРИД-ТИТАНОВЫХ ПОКРЫТИЙ ПРИ ЭЛЕКТРОННОМ ОБЛУЧЕНИИ

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В данной работе представлены экспериментальные результаты исследования структурных и фазовых изменений нитрид-титановых (TiN) покрытий при термическом и электронном облучении. Непрерывное электронное облучение покрытых образцов проводили на ускорителе ЭЛВ-4. Установлено, что электронное облучение с энергией электронов 1,3 МэВ и интегральной дозой облучения $0.52 \cdot 10^{19}$ е⁻/см² приводит к увеличению микротвердости покрытий TiN на 20%. Установлено, что основным фактором увеличения микротвердости покрытия после электронного облучения в вышеуказанных режимах является образование новых фаз, в частности интерметаллида Co_2Ti.

Ключевые слова: покрытие, твердость, электронное облучение, нитрид титана, структура.