JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 11 No 5, 05037(4pp) (2019)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 11 № 5, 05037(4cc) (2019)

# Tribotechnical Properties of (TiZr)N/(TiSi)N Multilayer Coatings with Nanometer Thickness

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(Received 27 April 2019; revised manuscript received 23 October 2019; published online 25 October 2019)

The tribotechnical characteristics of (TiZr)N/(TiSi)N nitride multilayer coatings obtained by the method of vacuum-arc deposition at room temperature were investigated. The analysis of the influence of the deposition conditions on the mechanical and tribological properties of coatings with different modulation periods (total bilayer thickness) of this structure was carried out: in the 1st series $\lambda$ about 20.4 nm, in the 2nd series with $\lambda \approx 43.9$ nm, and in the 3*d* series of samples the coating was formed with a thickness of $\lambda \approx 137$ nm. The results of wear were investigated, and they indicate that multi-element nitride coatings wear out by abrasive mechanism. The intensity of wear in coatings with the number of layers 360 (period $\lambda = 20.4$ nm) is 2 times lower than in coatings of 89 layers (period $\lambda = 137$ nm). The values of the friction coefficient were 0.79-0.82 during tests. Coating hardness was $HV_{0.05} = 37.6$ GPa for the samples of series 1, $HV_{0.05} = 31.2$ GPa for the second series, and $HV_{0.05} = 26.5$ GPa for the samples of series 3.

**Keywords:** Vacuum arc deposition, Multilayer nitride coatings, Structure, Friction coefficient, Hardness.

DOI: 10.21272/jnep.11(5).05037 PACS numbers: 61.46.– w, 62.20.Qp, 62-65.– g

## 1. INTRODUCTION

Analysis of the literature data shows that one of the ways to improve the physical-mechanical characteristics of coatings is the creation of multilayer structures with a nanometer-thick layer based on transition metal nitrides by transferring them to a nanostructured state [1, 2]. Due to the multilayer, as well as by integrating the properties of different layers, you can purposefully influence the structure and properties of the coatings, thereby improving the performance characteristics of products, in particular, cutting tools, machine parts, etc. [3, 4].

Literary data shows that addition of layers based on nitrides of zirconium, chromium, molybdenum, etc. to multilayer coatings based on titanium nitride leads to an increase of physical and mechanical properties, as well as operational characteristics [5].

Currently, Ti-Si-N multi-element composite coatings [6] have high values of hardness, thermal stability, and resistance to oxidation at high temperatures. Multilayer films layered on the basis of Ti-Si-N allow to increase the properties and significantly expand the field of application of protective coatings.

Therefore, the purpose of this work is to study the effect of nanometer layer thicknesses on the mechanical and tribological properties of multilayer nitride coatings of the (TiZr)N/(TiSi)N system.

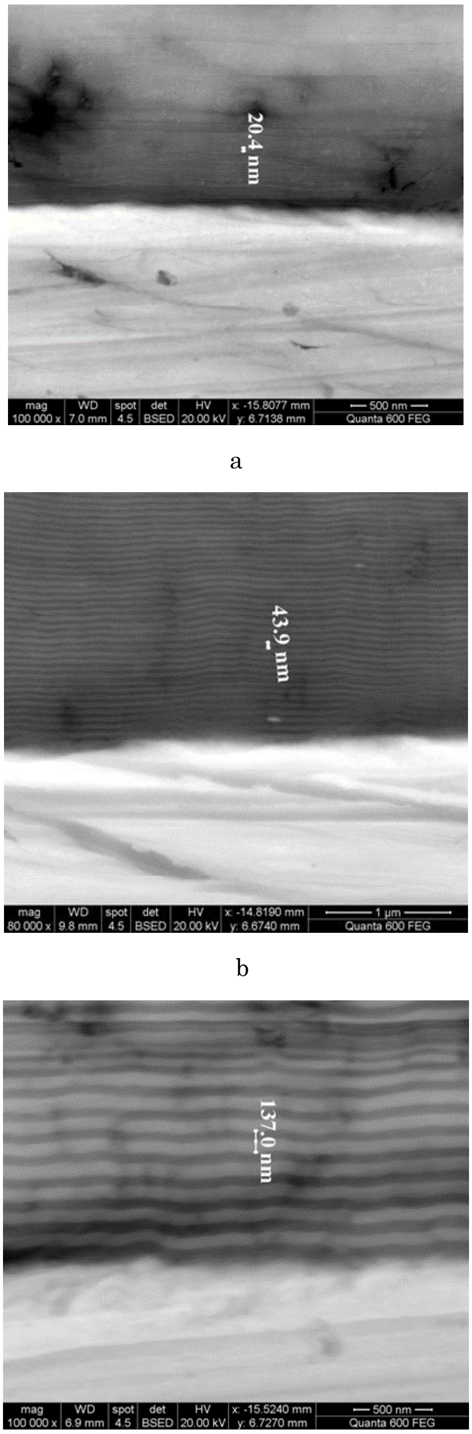
## 2. MATERIALS AND RESEARCH METHODS

(TiZr)N/(TiSi)N multilayer coatings were obtained by vacuum arc deposition. $Ti_{0.75}Zr_{0.25}$ and $Ti_{0.94}Si_{0.6}$ were used as evaporated materials. Coatings were deposited on the polished surface of samples made of 12X18H9T steel ($R_a = 0.09$ μm). Three series of coatings were obtained differing in the number of layers at a residual nitrogen pressure of $P = 0.66$ Pa, constant in magnitude and time, the negative bias potential supplied to the substrate ($U_b = -200$ V). The number of layers was: 360 for the 1st series, 180 for the 2nd series, and 89 layers for the 3rd series. The image of the surface of the coatings, as well as the elemental composition of the coatings, was determined using a Quanta 200 3D scanning electron microscope and FEI Nova NanoSEM 450. To determine the thickness of the coatings and layers on the coated steel plates, a cross section was made to the coating. The phase-structural state of the coatings was studied using a DRON-4M diffractometer with Cu-$K_\alpha$ radiation. Measurement of the microhardness of the coatings was carried out according to the micro-Vickers method with loads on an indenter of 50 g on a microhardness meter DM-8. Revetest scratch tester (CSM Instruments) was used to determine the adhesion/cohesion strength of the coatings, scratch resistance and fracture mechanism. The wear resistance of the coatings was studied using tribometry methods with a tribomic friction machine (CSM Instruments) according to the disk-ball scheme.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows the results of images of the lateral surface of (TiZr)N/(TiSi)N coating samples for 3 series, as well as elemental composition data (Table 1). For the first series of samples, the vapor layer had a thickness $\lambda \approx 20.4$ nm, for the 2nd series of (TiZr)N/(TiSi)N coating samples it was $\lambda \approx 43.9$ nm, and for the third series of coating samples thickness was $\lambda \approx 137$ nm (Fig. 1).

As can be seen from the results shown in Table 1, the nitrogen content in the coatings of series 1 and 2 is almost the same, but in the samples of series 3 the content of zirconium and titanium is higher and of nitrogen is lower. The increase of the titanium in the coating (series 3, the period of the layers was 137 nm) is probably due to a more efficient interaction of titanium atoms with nitrogen in the near-surface region. According to the literature [7], among the nitride coatings, the TiN system is the most stable, while the efficiency of its spraying from a growing surface (secondary spraying) is significantly reduced, which ultimately leads to its enrichment with a strong nitride-forming element (in this case, Ti).



a

b

c

**Fig. 1** – Image of the cross section of (TiZr)N/(TiSi)N multilayer coatings: a) for the first series with the number of layers 360; b) for the second series with the number of layers 180; and c) for the third series with the number of layers 89

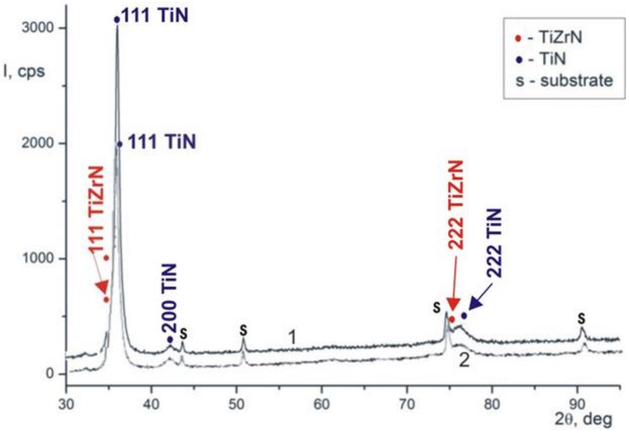


**Fig. 2** – Plot of diffraction spectra of (TiZr)N/(TiSi)N coatings: 1) series 1; 2) series 2

The presence of silicon in small amounts (Table 1), as well as the deposition conditions, do not allow the formation of $SiN_x$ phases [8], which was confirmed by the absence of peaks in the diffraction spectra (Fig. 2) related to these phases. The diffraction patterns of the coated samples contain lines from the substrate (steel). A strong (111) texture was revealed in all nitride phases, i.e., most grains are oriented by crystallographic (111) planes parallel to the surface of the coatings. The calculation of the substructural characteristics was carried out according to 2 orders of the reflection family (111) and (222). The structure of the obtained coatings is characterized by a high level of microdeformation of the lattice (Table 2). The obtained results indicate, probably, that the chemical composition in each phase of the coating is inhomogeneous. Coatings have a pronounced texture [111].

The microhardness of the coatings (the thickness of the resulting coatings was ~ 3.0 μm) was measured on samples. The average values (over ten measurements) of hardness are: $HV_{0.05} = 37.6$ GPa for samples of series 1 (360 layers), $HV_{0.05} = 31.2$ GPa for the second series (180 layers), and $HV_{0.05} = 26.5$ GPa for samples of series 3.

The tribotechnical characteristics of nitride multilayer coatings were studied at room temperature with a load of 6.0 N. The test results of (TiZr)N/(TiSi)N coatings deposited on steel disks made of steel 45 are shown in Table 3.

It is known that the coefficient of friction depends on the specific measurement technique [9]. On all coated samples, the coefficient of friction is quite high. This can be explained by the surface roughness (Table 3) associated with the presence of a droplet fraction formed by the vacuum-arc deposition method. Since in the future, when measuring the coefficient of friction, the wear products are not removed from the contact surface, the measured value of the coefficient of friction increases to 0.82.

Photos of the surface of the friction tracks and the general view of the counterbodies obtained using scanning microscopy and optical microscopy after testing are shown in Fig. 3.

The energy-dispersion spectrum of wear products is shown in Fig. 4 and the chemical analysis data is given in Table 4.

**Table 1** – The chemical composition of (TiZr)N/(TiSi)N multilayer coatings

| Coatings | Elements included in coatings, at. % | | | | |
|---|---|---|---|---|---|
| | N | Si | Zr | Ti | Fe |
| 1st series | 49.37 | 0.51 | 4.42 | 43.78 | 1.92 |
| 2nd series | 48.86 | 0.73 | 4.38 | 45.63 | 0.4 |
| 3rd series | 45.45 | 0.84 | 5.18 | 47.28 | 1.25 |

**Table 2** – Phase composition and substructural characteristics of (TiZr)N/(TiSi)N coatings

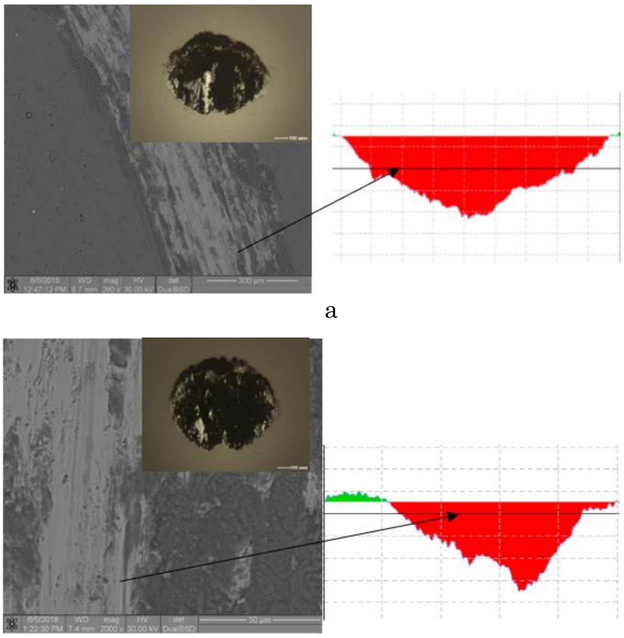
| Series No | Phase | Lattice parameter, nm | OCD size, nm | Microdistortion level |
|---|---|---|---|---|
| 1 | (TiZr)N | 0.4391 | Could not be determined | |
| | TiN | 0.4320 | 24.2 | $5.76\times10^{-3}$ |
| 2 | (TiZr)N | 0.4335 | 42.1 | $4.54\times10^{-3}$ |
| | TiN | 0.4287 | 23.9 | $5.04\times10^{-3}$ |
| 3 | (TiZr)N | 0.4356 | 61.1 | $3.88\times10^{-3}$ |
| | TiN | 0.4296 | 35.4 | $6.3\times10^{-3}$ |

**Table 3** – Tribological characteristics of multilayer nitride coatings of (TiZr)N/(TiSi)N systems

| Series | Coefficient of friction, μ | | Wear rate, $\nu$, $mm^3\times N^{-1}\times m^{-1}$ | | $R_a$, μm |
|---|---|---|---|---|---|
| | Elementary | During testing | Counterbody ($Al_2O_3$) | Coating | |
| 1st series | 0.62 | 0.82 | $3.2\times10^{-6}$ | $2.8\times10^{-5}$ | 0.15 |
| 2nd series | 0.64 | 0.81 | $1.45\times10^{-6}$ | $3.9\times10^{-5}$ | 0.18 |
| 3rd series | 0.53 | 0.79 | $2.4\times10^{-6}$ | $5.8\times10^{-5}$ | 0.21 |

**Table 4** – Chemical composition of wear products

| Coatings | Elements included in the composition of wear products, at. % | | | | | | |
|---|---|---|---|---|---|---|---|
| | N | O | Al | Si | Zr | Ti | Fe |
| 1st series | 13.32 | 45.53 | 0.71 | 18.53 | 0.97 | 7.18 | 13.77 |
| 2nd series | 12.11 | 44.81 | 0.4 | 21.52 | 0.74 | 5.85 | 14.43 |


a

b

**Fig. 3** – Image of the surface of the friction tracks of the coatings: a) 1 series; b) 2 series

The analysis of the surface of the friction tracks, as well as the data of the chemical analysis of the wear products, indicate that in the process of wear in the atmospheric environment, as well as by the dynamic interaction between the contacting materials, oxide films are formed on the coating surface [10, 11]. On the one hand, they protect the friction surface from wear, and, on the other hand, the products of oxidative wear can have greater hardness and cause abrasive wear.

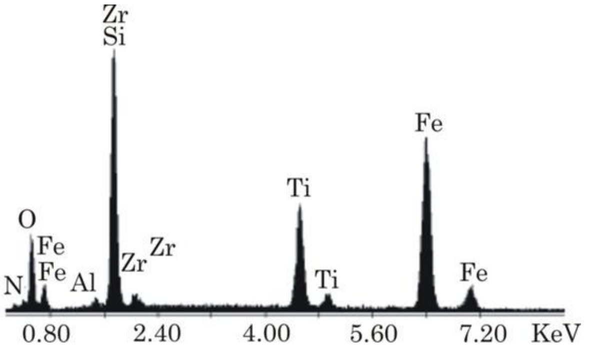


**Fig. 4** – Energy-dispersive spectrum of the friction track of the coating of series 1

Finally, we can draw such conclusions.

1. The multilayer nitride coatings based on the (TiZr)N/(TiSi)N system were obtained by vacuum arc deposition. It was shown that the coatings have two phases (Zr, Ti)N and TiSiN solid solutions with FCC crystal lattice (structural type NaCl).

2. The average values of hardness are the following: $HV_{0.05} = 37.6$ GPa for samples of series 1 (360 layers), $HV_{0.05} = 31.2$ GPa for the second series (180 layers), and $HV_{0.05} = 26.5$ GPa for samples of the 3rd series.

3. The intensity of wear of the coatings with the number of layers 360 (period $\lambda = 20.4$ nm) is 2 times lower than of coatings with 89 layers (period $\lambda = 137$ nm).

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# Триботехнічні властивості багатошарових покриттів (TiZr)N/(TiSi) N з нанометровою товщиною

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Досліджено триботехнічні характеристики багатошарових нітридних покриттів (TiZr)N/(TiSi)N, отриманих методом вакуум-дугового осадження при кімнатній температурі. Проведено аналіз впливу умов осадження покриттів на механічні та трибологічні властивості покриттів з різними періодами модуляції (загальна товщина двошарового шару) цієї структури: у 1-й серії з $\lambda$ близько 20.4 нм, у 2-й серії з $\lambda \approx 43{,}9$ нм, і в 3-й серії зразків формувалося покриття товщиною $\lambda \approx 137$ нм. Результати зносу були досліджені, і вони свідчать про те, що багатоелементні нітридні покриття зношуються за абразивним механізмом. Інтенсивність зносу в покриттях з кількістю шарів 360 (період $\lambda = 20{,}4$ нм) у 2 рази нижча, ніж в покриттях з 89 шарами (період $\lambda = 137$ нм). Значення коефіцієнта тертя під час випробувань становили 0,79-0,82. Твердість покриттів становила $HV_{0.05} = 37.6$ ГПа для зразків першої серії, $HV_{0.05} = 31.2$ ГПа для зразків другої серії та $HV_{0.05} = 26.5$ ГПа для зразків третьої серії.

**Ключові слова:** Вакуумне дугове осадження, Багатошарові нітридні покриття, Структура, Коефіцієнт тертя, Твердість.