

# Influence of the third element additives on the surface morphology of the wear-resistant ZrN coatings

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**Abstract.** ZrN, Zr-O-N, and Zr-Si-N wear resistant coatings were formed using vacuum-arc plasma fluxes deposition at the substrate bias voltage 100 V on HS6-5-2 steel substrates. For comparison, a sample of ZrN coating at the same substrate bias voltage on the same substrate was obtained using magnetron sputtering. The structural and mechanical properties were characterized using X-ray diffraction, atomic force microscopy, and nanoindentation. The influence of O and Si additives on the surface morphology of coating were investigated.

## 1. Introduction

One of the ways to improve the mechanical and tribological properties of machine parts is surface modification by a hard coating formation [1-4]. The transition metal nitrides coatings are widely applied for cutting tools and tribological surfaces [5,6]. The properties of two-component coatings can be improved by adding the third element or even more of them to the two-element system. ZrN coatings occupy a special place among the transition metal nitrides [7,8] and have a favorable combination of mechanical properties under conditions requiring high thermal stability.

The work is aimed at the study of the effect of Si and O addition on the surface morphology and such structure characteristics of ZrN coatings like lattice parameter, grain size on the surface, and roughness in microscale, at the same substrate bias voltage.

## 2. Experimental details

ZrN, Zr-O-N, and Zr-Si-N coatings were synthesized using cathodic arc evaporation (CAE) on HS6-5-2 steel substrates in a "Bulat-3T" system. The coatings were deposited at nitrogen pressure of 2 Pa. The deposition was performed at substrate bias voltage of -100 V. Zr-O-N coatings were deposited with relative oxygen concentration  $O_2(x) = O_2/(O_2+N_2)$  amounted to 10%. A substrate temperature was 450°C for ZrN and Zr-Si-N and 350°C for Zr-O-N. The deposition time was 30 min and thickness of the coatings was about 3 μm.

X-ray diffraction (DRON-3 M, Cu-Kα) was used to characterize the phase composition of the coatings. Lattice parameter and the average size of the crystallites of the ZrN phase were calculated according to (111) plane of the obtained diffraction patterns.



**Table 1.** The properties of ZrN, Zr-O-N, and Zr-Si-N coatings, investigated in this work: lattice parameter, crystallite size, Ra, size of grains on the surface, E, and H.

Number of samples	Content of samples	R <sub>a</sub> , nm 2x2 μm <sup>2</sup>	Lattice parameter, nm	Crystallite size, nm	Size of grains on the surface, nm	E, GPa	H, GPa
1	ZrN (CAE)	6.2±0.3	0.4595*	18±0.2	700	282±14	29±2
2	Zr-Si-N	5.2±0.3	0.4614	6±0.1	583	298±15	22±1
4	Zr-O-N	3.2±0.2	0.4615	15±0.2	300	312±16	31±2
5	ZrN (magnetron)	2.7±0.1	0.4608	11±0.1	100	307±15	29±2

\*According to PDF No 35-0753 for ZrN (ASTM), a = 0.4577 nm

Hardness and elastic modulus were determined using nanoindentation. Hysitron Ti 750 Ubi (USA) equipped with the Berkovich diamond indenter with tip radius of 150 nm was used. The standard fused quartz sample was used to control the calibration correctness of the device. The measurements were performed at the load of 10 mN.

The surface morphology of the coatings was investigated using atomic force microscopy (AFM) device HT-206 (produced by MTM Belarus) in the contact mode. AFM is the technique to simultaneously study different surface phenomena, like roughness of initial surfaces [9] or surfaces after mechanical [10,11] or chemical treatment [12,13], friction testing [14], and phase distribution [15]. The surface topography was studied using standard CSC38 silicon probe of beam type with the radius of tip curvature less than 10 nm and stiffness of cantilever of 0.08 N/m produced by “Mikromasch” (Estonia). The roughness of the surface in microscale was investigated in the area of 2×2 μm<sup>2</sup>.

The samples under study are listed in Table 1.

### 3. Results and discussion

According to the X-ray analysis, the addition of alloying elements to ZrN coating in small amounts (6 at.% Si or 10 % O in the working gas mixture) does not lead to formation of silicon containing or oxygen containing phases; the diffraction lines are shifted to lower angles from their positions.

The introduction of small amounts of additives into the ZrN lattice increases the lattice parameter to 0.4614 for Si atoms and to 0.4615 for O atoms. The introduction of additive atoms reduces the crystallite size in Zr-Si-N and Zr-O-N coatings. The average size of the crystallites in ZrN calculated for (111) plane is about 18.3 nm (Table 1). Silicon introduction into ZrN coating deposited at the same substrate bias voltage of –100 V results in a significant reduction in size of the crystallites to about 6.4 nm. Oxygen introduction into ZrN coating leads to reduction in size of the crystallites from 18 nm to about 15 nm. In the work [16], it was found that oxygen in ZrN coatings obtained by magnetron sputtering led to the crystallite size decrease. Similar values of crystallite sizes in magnetron sputtered coatings ranging from 10 to 12 nm were calculated for argon and nitrogen mixture during deposition. In this work, ZrN coatings deposited by magnetron sputtering at the same bias voltage (UB = –100 V) show a higher lattice parameter than ZrN coatings deposited by CAE equal to 0.4608. The average size of crystallites in the magnetron sputtered ZrN was about 11 nm (Table 1). That value was twice lower than in Ref. [17], where the average size of crystallites was about 22 nm and decreased to 2.5 nm for about 10 at.% of silicon.

The same values of hardness and elastic modulus of obtained coatings show that energetic levels (energy of ion bombardment) of different processes in this work were close to each other (Table 1). It is known that mechanical properties of the coatings deposited using CAE are better compared using

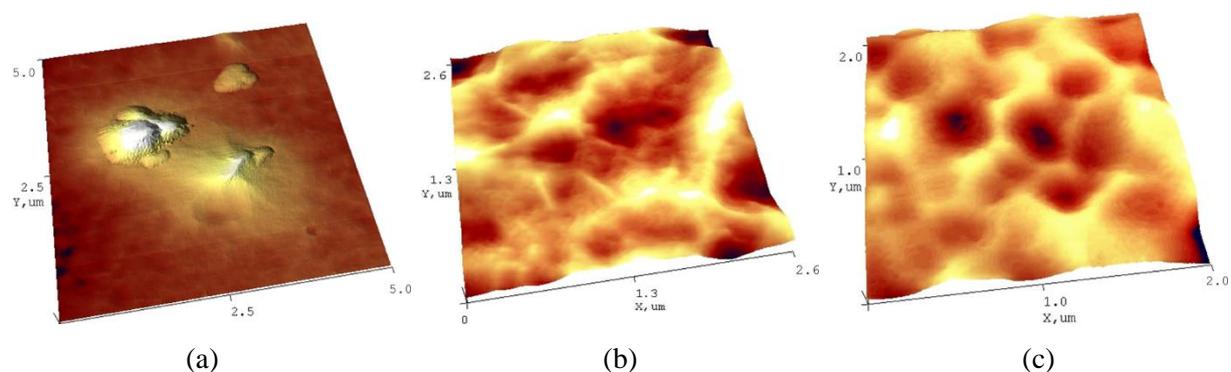
magnetron sputtering [8]. Such coatings also show the higher density. But in this research, H and E values in ZrN coatings obtained by CAE and magnetron sputtering are almost the same. The surface microstructure is one of the most important parameters of the wear resistant coatings.

ZrN, Zr-O-N, and Zr-Si-N coatings in the range of areas from  $100 \times 100 \mu\text{m}^2$  till  $10 \times 10 \mu\text{m}^2$  show classical surface microstructure characteristic for coatings deposited using PVD methods. The numerous craters and macroparticles are apparent on the coating surface (Fig. 1a). Microparticles in ZrN coating structure have two forms – circular and elongated. The difference in the shape is probably connected with the different phase content of the particles. The circular particles consist of the plates and have obvious boundary between the particle and the surface. Some particles in the form of separate plates are spread over the surface. The elongated microparticles represent a sort of thickened boundary of cells embedded in the surface. During study of nitride and oxinitride coatings microstructure, both structured features («smooth surface» and macroparticles) should be taken into account. Microparticles participate in the formation of the altered secondary structure, which appears in the friction contact under the action of the load and participates in the friction process. Microparticles in Zr-O-N coating deposited at  $O_{2(x)} = 10\%$  look like separate plates grouped together around the joint centre or around the elongated feature. There are particles looking like monolithic features. Using lateral forces AFM mode, it is possible to compare the microstructure of the smooth surface and the microplate position in the microparticle. So, according to the investigated microstructure, microparticles appear on the surface as a result of crystallization process of each plate, but not as a result of accidental hitting of microdrops and their solidification.

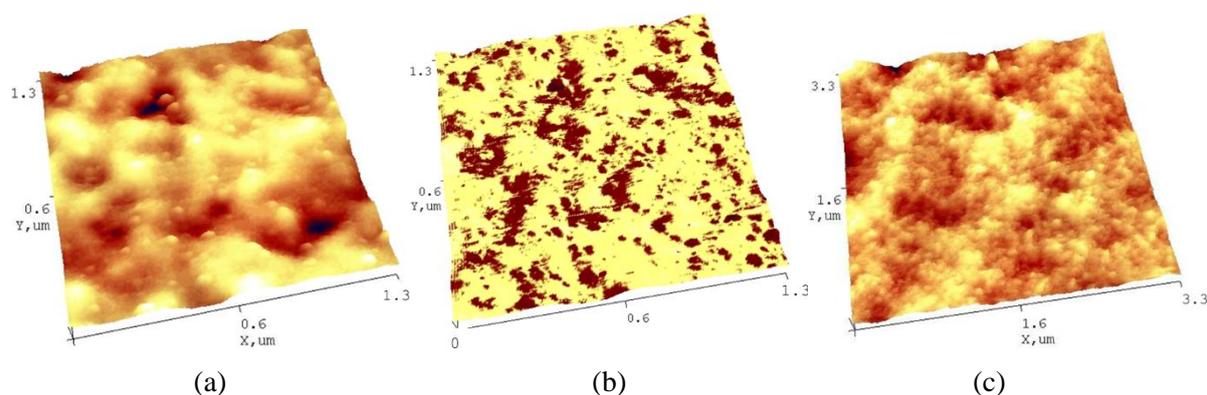
«Smooth surface» of ZrN coating obtained by AFM is interpreted as a multi-cell structure, in which elevated vertical grain boundaries are visible (Fig. 1b). The average size of cells is 700 nm. The coating microstructure of Zr-Si-N deposited at  $UB = -100$  V shows also the form of concave cells (Fig. 1c). The addition of Si into coating during deposition reduces the average size of cells from 700 to 583 nm. The roughness of smooth surface Zr-Si-N decreases from 6.2 to 5.2 nm for ZrN coating.

The addition of oxygen instead of Si reverses the microstructure of the surface (Fig. 2a). Cells are not visible. Rounded "large" crystallites with diameter of 300 nm appear. Rounding of faces and grain coarsening take place in comparison with ZrN. The surface looks like the ledges covered with a layer of film and are smooth because of this.  $R_a$  is 2.3 nm; there are no "elongated" forms. The lateral forces map reveals a significant difference between the round grains from the rest of the surface (Fig. 2b). Thus, the distribution over the surface of the oxide phases can be detected.

ZrN coating obtained by magnetron sputtering has surface microstructure, which is drastically different from ZrN coating obtained by CAE (Figs. 1b, 2c). It consists from the separate grains with diameter about 100 nm. The surface turns out to be more "friable", which agrees well with the results of work [17].



**Figure 1.** The topography of ZrN and Zr-Si-N coatings: (a) ZrN, scanned area  $4.9 \times 4.9 \mu\text{m}^2$ ; (b) ZrN, scanned area  $2.6 \times 2.6 \mu\text{m}^2$ ; (c) Zr-Si-N, scanned area  $2 \times 2 \mu\text{m}^2$



**Figure 2.** The surface of Zr-O-N and ZrN coatings, obtained by magnetron sputtering: (a) Zr-O-N, scanned area  $1.3 \times 1.3 \mu\text{m}^2$ ; (b) lateral forces map, scanned area  $1.3 \times 1.3 \mu\text{m}^2$ ; (c) magnetron ZrN coatings, scanned area  $3.3 \times 3.3 \mu\text{m}^2$ .

#### 4. Conclusion

X-ray did not detect the phases containing silicon and oxygen after doping ZrN coatings with small amount of additives (6 at.% of Si or 10% of  $\text{O}_{2(x)}$ ). All coatings had similar values of microhardness (22-31 GPa) and elastic modulus (282-312 GPa). Coatings with small additions of Si and O showed the close parameters of the crystal lattice.

The presence of the additional elements during the formation of ZrN coating changed the morphology of the coating surface. Thus, the initial structure of ZrN coating obtained by the CAE had a honeycomb structure with the average cell size of 700 nm. The addition of 6 at% Si reduced the cell size to 583 nm. The addition of oxygen changed the cellular structure to a smoothed one with circular grains with diameter of 300 nm. The contrast in lateral forces AFM mode allowed us to assume that the oxide phases were in Zr-O-N coating. The method of magnetron sputtering at the same bias voltage on the substrate formed a less dense grain microstructure of the surface with a grain size of 100 nm.

Modification of ZrN coatings with the small amounts of Si and O additives allows forming the surfaces for tribological application with different types of microstructure and, hence, properties of the surface layer in comparison with a pure ZrN coating.

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