

Comparison of corrosion, physico-mechanical and wear properties of TiN, ZrN, $Ti_xZr_{1-x}N$ and $Ti_{1-x}Al_xN$ coatings

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Abstract. In this paper, TiN, ZrN, $Ti_xZr_{1-x}N$, $Ti_{1-x}Al_xN$ coatings were obtained by cathodic arc evaporation at optimal technological parameters. The corrosion properties of these coatings were investigated in 5% NaOH. The coating ZrN deposited by cathodic arc evaporation slows down the corrosion in the 5% NaOH by over 3,000 times, and the passive current – by 2,000 times. The $Ti_xZr_{1-x}N$ coating has the best physico-mechanical properties: microhardness $H = 36$ GPa, Young's modulus $E = 312$ GPa, elastic recovery $W_e = 78$ %, resistance to elastic failure strain $H/E = 0.12$, and resistance to plastic strain $H^3/E^2 = 1.31$ GPa. The $Ti_{1-x}Al_xN$ coating has the best wear properties: friction coefficient 0.09, counterbody wear intensity by volume $0.43 \cdot 10^{-8}$ mm³/Nm, coating wear intensity by volume $0.05 \cdot 10^{-4}$ mm³/Nm and by mass $0.03 \cdot 10^{-5}$ mg/Nm. Multilayer coating TiN- $Ti_xZr_{1-x}N$ - $Ti_{1-x}Al_xN$ -ZrN (ZrN-top layer) has a complex of high physico-mechanical and wear properties in 5% NaOH.

1 Introduction

Operating experience and test results of cutting tools and friction pairs show that their premature failure, as a rule, caused by low wear-resistant, corrosive and physico-mechanical (functional) properties of their materials in the friction zone. Single-layer coatings more often do not possess a set of these functional properties [1-4]. This prompted researchers to create multilayer nanostructured coatings that improve the durability of tools and friction pairs under conditions of exposure to abrasive, thermal, power loads and an aggressive environment. The choice of material for the layers of multilayer coatings is a complex task.

The article aim is to study the corrosion, physico-mechanical and wear properties of TiN, ZrN, $Ti_xZr_{1-x}N$ and $Ti_{1-x}Al_xN$ coatings deposited by the cathodic arc evaporation (CAE) method at optimal technological parameters.

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2 Material and methods

The TiN, ZrN $Ti_xZr_{1-x}N$ $Ti_{1-x}Al_xN$ coatings, chosen as model ones, were formed by the cathodic arc evaporation (CAE) on automated unit URM3.279.048 equipped with two evaporators and four DC magnetron sputters. Optimal technological parameters of the deposition process are shown in Table 1.

Aluminum of technical purity EN AW-1085 was used as a material of low-melting cathode: Al-99.85 wt.%, Si-0.06 wt.%, Fe-0.08 wt.%, Cu-0.01 wt.%, Mn-0.02 wt.%, Mg-0.02 wt.%, Zn-0.02 wt.%, Ga-0.02 wt.%, Ti-0.008 wt.%, Others each 0.02 wt.%). The refractory cathode material was titanium of technical purity ERTi-1: Ti -99.42 wt.%, Si-0.08 wt.%, Fe-0.2 wt.%, C-0.05 wt.%, O-0.1 wt.%, N-0.04 wt.%, H-0.008 wt.%, Others each 0.1 wt.%. The refractory cathode material was zirconium of technical purity R60702 (ASTM B495): Zr- 94.7%; Hf – up to 4.5%; C-0.05 wt.%, O-0.16 wt.%, N-0.02 wt.%, H-0.004 wt.%).

Table 1. The formation processes parameters of the coating
 TiN, ZrN $Ti_xZr_{1-x}N$ $Ti_{1-x}Al_xN$.

Coating material	TiN/ZrN	$Ti_xZr_{1-x}N$	$Ti_{1-x}Al_xN$
Cathode material	Ti/Zr	Ti and Zr	Ti and Al
The gas mixture pressure of argon and nitrogen, Pa	1.0		
The ratio of Ar/N ₂ in the gas mixture, %	20:80	20:80	50:50
Arc current, A	90	90	75
Bias voltage, B	200		
Cathode-substrate distance, mm	310±20		
Ti/Zr sublayer deposition time, min	10		
TiN, ZrN, $Ti_xZr_{1-x}N$ and $Ti_{1-x}Al_xN$ coating deposition time, min	30		
Test sample	material	hard alloy HG30	
	size, mm	10x10x3	

The substrate rotation speed during the deposition of the $Ti_{1-x}Al_xN$ coating was 20 m/s.

Electrochemical tests (polarization curves, electrochemical impedance spectroscopy (EIS)) were performed in 5% NaOH. Coating defects can be more detectable in a NaOH solution due to the more significant dissolution of hard alloy in alkaline media [5]. The electrodes for electrochemical measurements were embedded in epoxy, leaving only one side of the sample in contact with the solution. Electrode surface was cleaned with ethanol and washed in the working solution. Polarization and impedance data on electrodes were measured at room temperature (22–24 °C) in a three-electrode cell in unstirred solutions without deaeration. The electrodes were inserted into a solution and the open-circuit potential was monitored until a steady-state potential was achieved. The impedance spectrum was measured initially at the open-circuit potential in the frequency $\omega/2\pi$ range from 30 kHz to 0.003 Hz with Solartron 1255 frequency response analyzer and Solartron 1287 potentiostat (Solartron Analytical). Then the impedance was measured at anodic polarization in the frequency range from 10 kHz to 0.01 Hz. The amplitude of the ac signal was 10 mV, and the duration of the current stabilization at each potential before impedance spectrum measurement was 10 min. The CorrWare, ZPlot, CorrView and ZView software (Scribner Associates, Inc.) was used for the measurements and data processing. The electrode potentials E are reported with respect to the standard hydrogen electrode [6-7].

The corrosion potential (E_{corr}), the polarization resistance (R_p), the corrosion current densities ratio for uncoated and coated substrate ($i_{corr,s}/i_{corr,c}$ – corrosion inhibition effect) and that of passive current densities for the same samples ($i_{p,s}/i_{p,c}$ – coating surface passivation degree) were determined to characterize the corrosion protection efficiency of

coatings. The polarization resistance was found from impedance data as the limit of the real part of impedance at $\omega \rightarrow 0$ minus the solution resistance [8]. The corrosion current densities i_{corr} were determined by extrapolation of cathodic and anodic parts of polarization curves to the corrosion potential. The passive current densities i_p were directly taken from the anodic polarization curves [6-7].

Physical-mechanical properties of coatings, including hardness H , elasticity modulus E , ratio H/E proportional to cracking resistance, ratio H^3/E^2 proportional to plastic deformation resistance, and elastic recovery W_e were determined in accordance with the standard DINENISO 14577-1 by a FISCHERSCOPE H100C hardness measurement system [9-10].

Friction behavior of coatings – friction coefficient f and torque M , counterbody wear intensity by volume I_c^v , counterbody wear rate V_c , and wear behavior of coatings – coating wear intensity by volume I_{coat}^v and by mass I_{coat}^m were described in [11-12].

3 Results and discussion

Corrosion, physico-mechanical, wear properties of TiN, ZrN, $Ti_xZr_{1-x}N$, $Ti_{1-x}Al_xN$ coatings deposited at optimal technological parameters are presented in Table 2. The diagrams of corrosion, physico-mechanical, wear properties of coatings, depending on their materials, are shown in Figures 1-3.

Table 2. Corrosion, physico-mechanical, wear properties of the coatings TiN, ZrN, $Ti_xZr_{1-x}N$, $Ti_{1-x}Al_xN$.

Properties value	Material and number of coating			
	TiN	ZrN	$Ti_xZr_{1-x}N$	$Ti_{1-x}Al_xN$
	1	2	3	4
Corrosion properties [6,7,13-17]				
$-E_{corr}, V$	0.10	0.14	0.32	0.40
$R_p, k\Omega \text{ cm}^2$	3300	1200	48	20
$i_{corr,s} / i_{corr,c}$	652	3190	325	10
$i_{p,s} / i_{p,c}$	643	2180	330	8
Physico-mechanical properties [9-18]				
H	36	30	36	32
E	387	314	312	329
H/E	0.09	0.10	0.12	0.1
H^3/E^2	1.31	0.46	1.31	0.7
W_e	64	62	78	68
Wear properties [19-20]				
f	0.08	0.06	0.07	0.09
$I_{coat}^m \cdot 10^{-5}, \text{mg/N}\cdot\text{m}$	3.54	6.86	0.86	0.03
$I_{coat}^v \cdot 10^{-4}, \text{mm}^3/\text{N}\cdot\text{m}$	0.08	0.92	0.08	0.05
$I_c^v \cdot 10^{-4}, \text{mm}^3/\text{N}\cdot\text{m}$	0.43	0.91	0.18	0.12

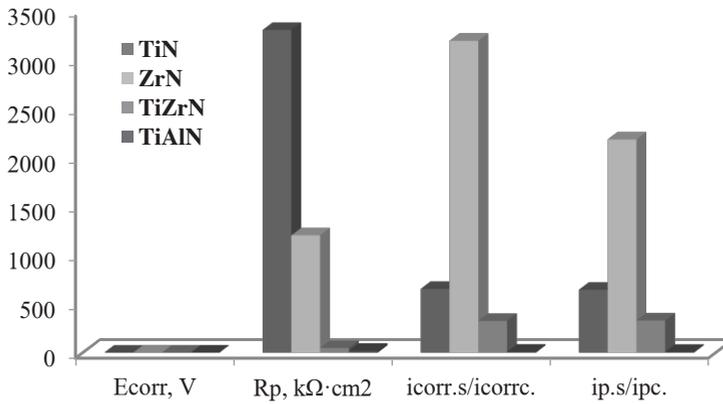


Fig. 1. Corrosion properties of TiN, ZrN, $Ti_xZr_{1-x}N$ and $Ti_{1-x}Al_xN$ coatings in 5% NaOH solution.

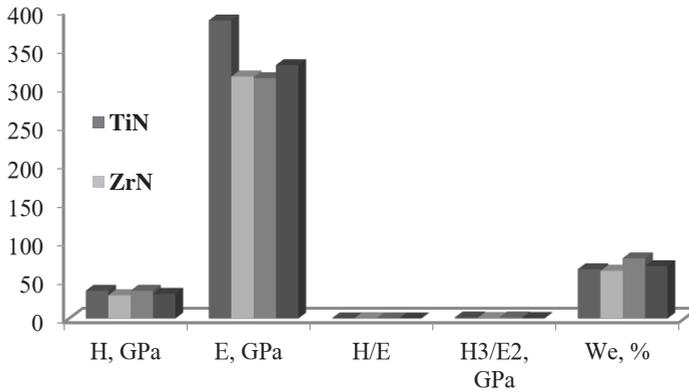


Fig. 2. Physico-mechanical properties of TiN, ZrN, $Ti_xZr_{1-x}N$ and $Ti_{1-x}Al_xN$ coatings.

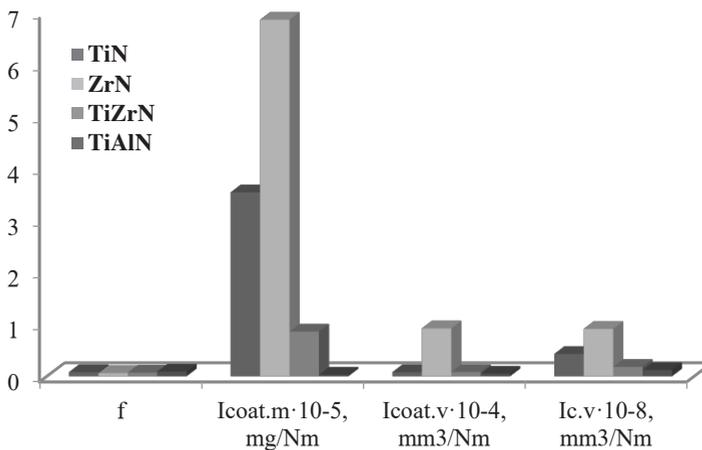


Fig. 3. Wear properties of TiN, ZrN, $Ti_xZr_{1-x}N$ and $Ti_{1-x}Al_xN$ coatings.

4 Conclusion

It was found that a multilayer coating, consisting of a TiN sublayer with a minimum corrosion rate and maximum adhesion strength to the surface of the cutting tool and a friction pair, the first $Ti_xZr_{1-x}N$ layer with a high elastic deformation capacity, and the second $Ti_{1-x}Al_xN$ layer with the best wear resistance and a top layer of ZrN with a better ability to reduce the corrosion current density and the corrosion rate in 5% NaOH, will allow to increase the performance of the cutting tool and friction pairs under high loading in an aggressive environment.

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