

Corrosion properties of zirconium-based ceramic coatings for micro-bearing and biomedical applications

J Walkowicz¹, V Zavaleyev¹, E Dobruchowska¹, D Murzynski¹, N Donkov^{2,5},
A Zykova³, V Safonov³ and S Yakovin⁴

¹Institute of Technology and Education, Koszalin University of Technology,
2 Sniadeckich str., 75453 Koszalin, Poland

²Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences,
72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria

³National Science Center, Kharkov Institute of Physics and Technology,
1 Academicheskaya str., 61108 Kharkov, Ukraine

⁴Department of Physical Technologies, Kharkov National University,
4 Svobody Sq., 61077 Kharkov, Ukraine

E-mail: nikolaid@abv.bg

Abstract. Ceramic oxide ZrO₂ and oxynitride ZrON coatings are widely used as protective coatings against diffusion and corrosion. The enhancement of the coatings' mechanical properties, as well as their wear and corrosion resistance, is very important for their tribological performance. In this work, ZrO₂ and ZrON coatings were deposited by magnetron sputtering on stainless steel (AISI 316) substrates. The adhesion, hardness and elastic properties were evaluated by standard methods. The surface structure of the deposited coatings was observed by electron scanning microscopy (SEM) and atomic force microscopy (AFM). The composition of the coatings was analyzed by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS). The corrosion resistance properties were evaluated using the potentiodynamic method. The results show that the corrosion parameters are significantly increased in the cases of both oxynitride and oxide coatings in comparison with the stainless steel (AISI 316) substrates.

1. Introduction

Novel functional coatings are widely used in different industrial areas for tribological applications [1]. The modification of metal materials by means of ceramic coatings deposition is an effective way of forming alternative bearing surfaces. Moreover, many such applications require a high stability in an aggressive and corrosive environment.

Wear and corrosion are the major processes that cause problems with metals and alloys [2]. Corrosion in the aqueous medium of human body fluids takes place via electrochemical reactions [3]. The body fluid environment may decrease the fatigue strength of the metal implant and enhance the release of iron, chromium, nickel, titanium ions, which are found to be powerful allergens and carcinogens [4]. Failure of metal products have been reported due to stress corrosion cracking and poor wear resistance [5,6]. The release of wear and corrosion debris and further accumulation of

⁵ To whom any correspondence should be addressed.



harmful products in internal organs of animals were observed in *in vivo* tests [7]. The corrosion and wear resistance properties of modern coatings will play a key role in future effective applications for micro-bearing and biomedical needs.

The aim of the present work was to study the effect of the compositional, structural and morphological properties of oxide ZrO₂ and oxynitride ZrON films on the mechanical and corrosion characteristics of the ceramic coatings prepared.

2. Materials and methods

The process of ZrO₂ and ZrON coatings deposition by magnetron sputtering was performed in a high-vacuum pumping system with a base pressure of about 10⁻³ Pa.

Stainless steel (AISI 316) discs with a diameter of 32 mm and a thickness of 3 mm were used as substrates. The substrates were successively ultrasonically cleaned in acetone, ethanol and deionized water and dried.

The magnetron discharge power was 4 – 5 kW. An ICP source for oxygen activation with RF power up to 1 kW was used. The target consisted of pure zirconium. The main parameters of the deposition process were the following: Ar pressure $P_{ar} = 2.3 \times 10^{-1}$ Pa, oxygen mass flow rate $q = 35$ sccm for ZrO₂ deposition and nitrogen mass flow rate $q = 27$ sccm for ZrON deposition, magnetron voltage $U_m = 500 - 520$ V, magnetron current $I_m = 7.0 - 7.6$ A, total pressure $P = 2.8 - 3.0 \times 10^{-1}$ Pa, coating deposition rate 6 – 8 μm/hour. An ion source was used for cleaning the samples' surface before deposition. More details on the magnetron and the ion source in the sputtering chamber were given previously in [8,9].

The thickness of the as-deposited coatings was measured by a Calotest device. The adhesion properties, hardness and elastic modulus were evaluated by standard methods by using a Revetest (CSM Instrumets) device; the Rockwell test was carried out by a type C diamond Rockwell indenter. To determine the micro-hardness, a Fischerscope® HM2000 tester was used. The surface roughness parameters, such as the arithmetic average roughness (R_a) and mean roughness depth (R_z) were measured by a Hommel Werke T8000 profilometer. The coatings' thickness and roughness parameters are presented in table 1.

Table 1. Characteristics of deposited coatings.

Material/Coating type	Roughness parameters		
	R_a [μm]	R_z [μm]	Thickness [μm]
(AISI 316) / ZrO ₂	0.145	0.849	1.0
(AISI 316) / ZrON	0.129	0.807	0.8

The surface morphology and topography were observed by a JSM 5500 LV electron scanning microscope and by atomic force microscopy (AFM). X-ray photoelectron spectroscopy (XPS) was carried out using an ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5×10⁻⁸ Pa (1×10⁻⁶ Pa during the measurement) with an Al Kα X-ray source (excitation energy $h\nu = 1486.6$ eV). The instrumental resolution measured as the full width at half maximum (FWHM) of the Ag3d5/2 photoelectron peak was 1 eV [9]. The composition of the coatings was analyzed by energy dispersive X-ray (EDX) spectroscopy (Oxford Link ISIS 300).

For the potentiometric study, all samples were washed in ethanol in an ultrasonic bath before the measurements. The active area of the sample was 0.287 cm². All samples were kept in contact with the electrolyte (0.9% isotonic NaCl solution, volume of the electrolyte 50 ml) for 1 hour before the measurements. The potential was in the range 0.7 – 0.8 V for the reference sample and 0.5 – 1.0 V for all samples with deposited coatings, the sweep rate was 1 mV/s, and the reading density, 3 mV. The temperature during the measurements was kept at 25 ± 1 °C. The values of the corrosion potential and the corrosion current density was estimated using the Tafel slopes extrapolation method.

3. Results and discussion

The composition of the ZrO_2 and ZrON coatings was analyzed by XPS and the photoelectron spectra of $\text{Zr}3d$, $\text{O}1s$, $\text{N}1s$ coatings were observed. Two peaks can be seen in the $\text{Zr}3d$ XPS spectrum, the first one being observed at the binding energy position $E = 182.4$ eV, and the second one exhibiting an energy shift of 2.43 eV away from the $3d$ level due to the spin-orbit coupling (figure 1a). The $\text{N}1s$ peak was detected at a binding energy of $E = 396.2$ eV, associated with the Zr-N chemical bond. In addition, a weak $\text{N}1s$ peak at a binding energy of $E = 398.0$ eV was recorded, corresponding to Zr-N-O chemical bonds. The $\text{O}1s$ high-resolution spectra demonstrated a peak at the binding energy position $E = 530.2$ eV, associated with the Zr-O chemical bond.

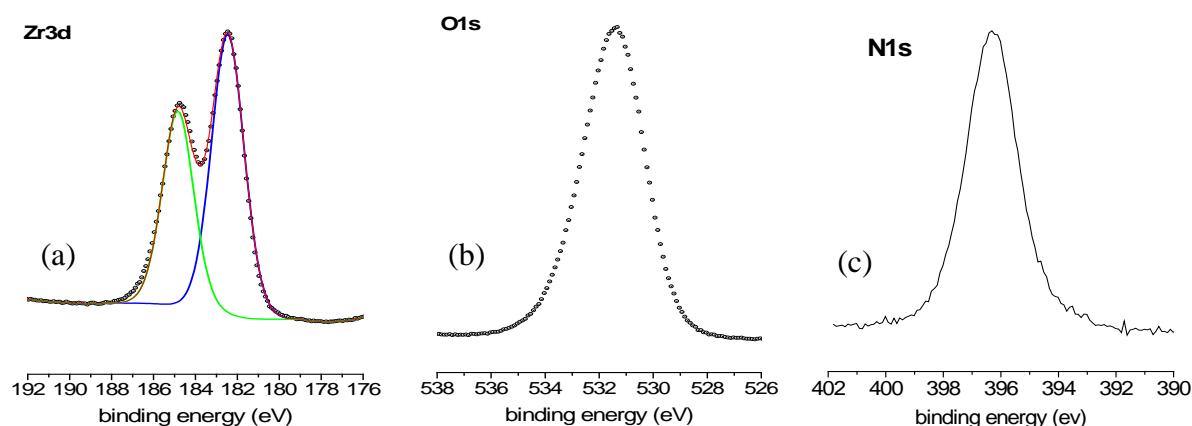


Figure 1. XPS spectra of Zr based coatings: (a) $\text{Zr}3d$, (b) $\text{O}1s$, (c) $\text{N}1s$.

The elemental compositions of the magnetron-sputtered coatings were investigated by energy dispersive X-ray (EDX) spectroscopy. The EDX spectra of the as-deposited coatings were in a good agreement with the XPS data. The elemental compositions of the ZrO_2 and ZrON coatings are presented in table 2.

Table 2. Elemental composition of the deposited coatings.

Element	Zr	Nb	Cr	Fe	O	N	Ar	Total
ZrO_2								
Weight %	64.11	3.08	1.25	4.14	27.05		0.37	100
Atomic %	27.74	1.31	0.95	2.93	66.71		0.37	100
ZrON								
Weight %	68.82	3.89	3.97	8.82	4.43	9.75	0.32	100
Atomic %	31.12	2.95	3.71	7.57	15.82	38.46	0.37	100

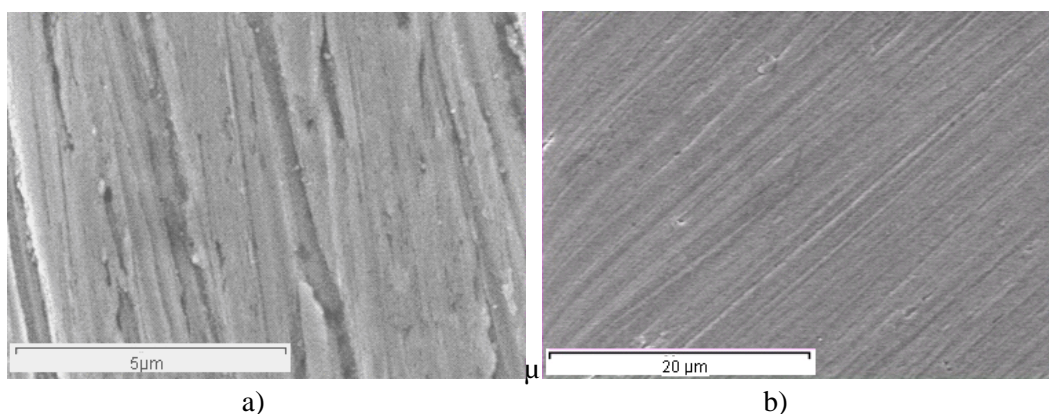


Figure 2. SEM micrographs of ZrO_2 (a) and ZrON (b).

The surface topography and morphology of ZrO_2 and ZrON coatings were investigated by electron scanning microscopy (figure 2). The surfaces of the deposited coatings have smooth relief with a uniform cross-section structure.

The mechanical properties of the coatings are the hardness H and effective Young's modulus E^* . The films' mechanical behavior is characterized by the ratio H/E^* [10,11], which is proportional to the film's fracture toughness and to the material's resistance to plastic deformation. There is a correlation between the coatings' mechanical properties and structure. The formation of oxynitride coatings improves the mechanical properties of the coated materials. The hardness parameters increase in comparison with the oxide films. The mechanical parameters of ZrO_2 and ZrON coatings deposited on the stainless steel samples (AISI 316) substrates are presented in the table 3.

Table 3. Mechanical characteristics of oxide and oxynitride coatings deposited on stainless steel (AISI 316) substrates.

Material/Coating	Mechanical parameters (average results 10 tests)			
	Hardness HV [GPa]	Young Modulus [GPa]	H/E^*	Adhesion [N]
AISI 316 / ZrO_2	14.5	133.7	0.1	17.1
AISI 316 / ZrON	15.7	132.8	0.11	19.6

The wear resistance properties of the obtained coatings are very important for applications as bearings [12,13]. Tribological tests were conducted previously [14]. The abrasive wear exhibited a minimum value of about $1.2 \times 10^{-4} \text{ mm}^3/\text{Nm}$ in the case of oxynitride coatings.

We further present corrosion tests of anodic polarization carried out by a potentiodynamic method in the potential range 0.5 – 1.0 V at a scanning rate of 1 mV/s. The corrosion behavior was analyzed of stainless steel samples (AISI 316), stainless steel substrates with ZrO_2 (figure 3a) and ZrON (figure 3b) coatings after corrosion tests at a temperature $25 \pm 1^\circ \text{C}$ in an isotonic NaCl (0.9%) solution. The values of the corrosion potential (E_{cor}) and the corrosion current density (J_{cor}) are presented in table 4.

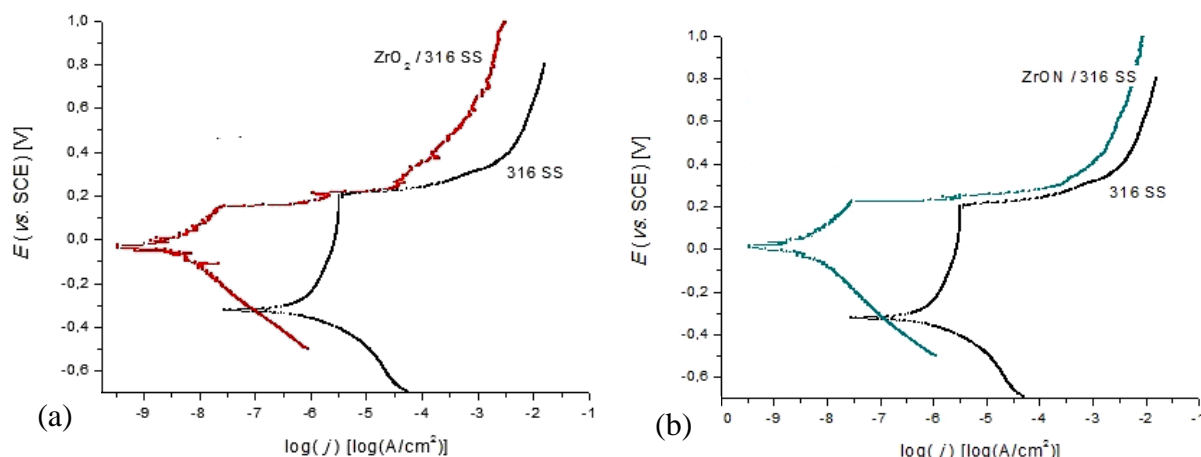


Figure 3. Corrosion resistance of stainless steel samples (AISI 316), stainless steel substrates with ZrO_2 (a) and ZrON (b) coatings after corrosion tests in an isotonic NaCl (0.9%) solution.

The results demonstrate the improvement of the corrosion characteristics of stainless steel samples coated by ceramic coatings. The corrosion resistance parameters increased in the cases of both oxynitride and oxide coatings.

The surface topography and morphology of stainless steel samples (AISI 316), stainless steel substrates with ZrO_2 and ZrON coatings after corrosion tests were analyzed by atomic force microscopy (figure 4).

The surface failure after a corrosion test in an isotonic NaCl (0.9%) solution further confirmed the main results as obtained from the polarization curves.

Table 4. Corrosion characteristics of oxide and oxynitride coatings deposited on stainless steel (AISI 316) substrates.

Material/ Coating	Corrosion potential E_{cor} (V)	E_v (V)	Corrosion current density J_{cor} (A/cm ²)
AISI 316	-0.312	0.208	8×10^{-7}
AISI 316 / ZrO ₂	-0.023	0.150	3×10^{-9}
AISI 316 / ZrON	0.015	0.224	4×10^{-9}

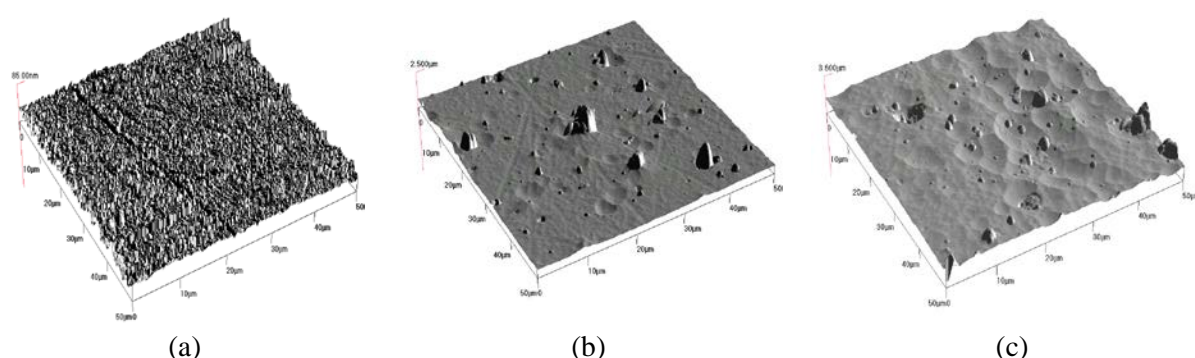


Figure 4. AFM images of stainless steel samples (AISI 316) (a), stainless steel substrates with ZrO₂ (b) and ZrON (c) coatings after corrosion tests in an isotonic NaCl (0.9%) solution.

4. Conclusions

A technology was developed allowing one to deposit oxide and oxynitride coatings with high hardness parameters up to 15 GPa and enhanced corrosion resistance characteristics on AISI 316 stainless steel substrates. The formation of oxynitride coatings improves the mechanical properties in comparison with the oxide films. The results show that both the oxide and oxynitride ceramic coatings possess excellent corrosion resistance characteristics towards an isotonic NaCl (0.9%) solution. The development of new low-cost and innovative bearing surfaces with advanced corrosion characteristics is very promising in view of biomedical applications, such as micro-bearings and joints replacement.

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