Tribological performance of ceramic coatings deposited on metal surfaces for micro-bearing biomedical applications

N Donkov¹, A Zykova², V Safonov², J Smolik³, R Rogowska³, V Luk’yanchenko⁴ and S Yakovin⁵

¹Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences, Sofia, Bulgaria
²Kharkov Institute of Physics and Technology, National Science Center, Kharkov, Ukraine
³Institute for Sustainable Technologies, National Research Institute, Radom, Poland
⁴Inmasters Ltd., Kharkov, Ukraine
⁵Department of Physical Technologies, Kharkov National University, Kharkov, Ukraine

E-mail: v_safonov@kipt.kharkov.ua

Abstract. Modification of metal materials by means of ceramic coating deposition is an effective way of forming alternative bearing surfaces. Ceramic AlN, Al₂O₃ and nanocomposite oxynitride coatings are widely used as protective coatings against wear, diffusion and corrosion. The enhancement of the mechanical properties, such as hardness parameters, effective Young’s modulus, toughness, elastic recovery and wear resistance of the coatings, is very important for the tribological performance of the next generation of ceramic-coated ball bearing devices.

1. Introduction
The formation of excessive amounts of metal wear debris, which cause osteolysis followed by loosening of the prosthesis, has brought about a renewed interest in metal bearings and module joint arthroplasty [1-3]. Modification of metal materials by means of deposition of ceramic coating is an effective way of forming alternative bearing surfaces. Ceramic AlN, Al₂O₃ and nanocomposite oxynitride coatings are widely used as protective coatings against wear, diffusion and corrosion [4-6]. The corrosion and wear resistance properties of modern coatings should be accurately tested in view of effective biomedical applications. It is necessary to evaluate the effect of the process variables, such as substrate preparation, surface texture, technological parameters and post-coating treatments, as these influence the tribological performance of the coatings. The successful application of ceramic coatings on metal bearing devices requires a further enhancement of the mechanical properties, such as hardness and effective Young’s modulus.

2. Materials and methods
The aim of the study was to analyze the wear mechanism while focusing on the tribological and mechanical properties of the bearing surfaces. We conducted a thorough investigation to evaluate the
tribological parameters of the oxide and composite nitride/oxide coatings. The substrates were load-bearing materials, namely, a titanium-based alloy (Ti4Al6V) and stainless steel (1H18N9).

Al2O3, AlN and composite nitride/oxide AlN/Al2O3 coatings were deposited using a coating apparatus equipped with a high-vacuum pumping system with a base pressure of about 10−3 Pa. The current-voltage characteristics (CVC) of the magnetron discharge for different oxygen and nitrogen flow rates are presented in figure 1. In the experiments, the argon pressure was kept constant at 1.8×10−1 Pa.

The coatings were deposited at the following process parameters: magnetron discharge power 1−4 kW; power of the activated oxygen source up to 1 kW; Ar pressure \( p_{\text{Ar}} = 1.8 \times 10^{-1} \) Pa; oxygen flux \( q = 30 \) sccm; nitrogen flux \( q = 23.5 \) sccm; magnetron voltage \( U_m = 570 \) V; magnetron current \( I_m = 8 \) A; total pressure \( p = 2.2 \times 10^{-1} \) Pa. Under these conditions, the coating deposition rate achieved was 8 \( \mu \)m/hour. An ion source was used for etching and cleaning the surface of the samples before the deposition of the ceramic coatings.

Figure 1 presents the current-voltage characteristics of the magnetron with targets of aluminum in a mixture of argon with oxygen or nitrogen at various reactive gas flows.

![Figure 1. CVC of the magnetron discharge for different flows of oxygen (a) and nitrogen (b), argon pressure \( p_{\text{Ar}} = 1.8 \times 10^{-1} \) Pa.](image)

The optimum deposition conditions were realized for the upper part of the CVC curves of the magnetron discharge in argon for both the oxygen and nitrogen gases.

The coatings’ adhesion properties, the hardness and the elastic modulus were evaluated by standard methods with the use of a Revetest (CSM Instruments) and a Rockwell indenter with a tip radius of 200 \( \mu \)m, within the load range of 200 N. X-ray diffraction patterns of Al2O3, AlN and composite coatings were taken by a DRON-3 diffraction device with filtered Cu-Ku radiation. X-ray photoelectron spectroscopy was carried out using an ESCALAB MkII (VG Scientific) electron spectrometer. The coating surface structure and morphology was estimated by means of a JEM 2100 scanning electron microscope (SEM) and an atomic force microscope (AFM, Quesant Instrument Corporation, USA).

Wear and abrasion resistance tests were performed on a CAT-S-AE (CSM Instruments) micro-scale abrasion tester. A 25-mm diameter micro-blasted ball of hardened steel (SAE 52100, 61 ± 2 HRC, \( R_a = 2.5 \pm 0.3 \) \( \mu \)m) was used as a counterpart. Suspensions of diamond, corundum and SiC particles (mean size 2−4 \( \mu \)m) were used as abrasive slurries for the tests. The rotation speed of the ball was set so as to provide a linear velocity of 0.1 m/s in all tests. The abrasive wear coefficient of the composite ceramic coatings was estimated according to a methodology described elsewhere [7, 8].

3. Results and discussion

The structure of the oxide and the composite magnetron-sputtered thin films was investigated by means of XPS and XRD. The X-ray diffraction patterns of the deposited coatings revealed a low crystallinity. After annealing at 800 ℃, a crystalline phase appeared with the major Al2O3 peaks
corresponding to (311), (222), (400), (440), and the AlN peaks corresponding to (100), (002), (101), (102), (110) reflections. A structural analysis of the coatings by means of XPS was also conducted [9]. The photoelectron spectra of Al2p, O1s, N1s and C1s were observed confirming the stoichiometric composition of the compound. The surface morphology was investigated by means of AFM and SEM. The surface of the Al2O3 coatings had a smooth relief with a uniform cross-section structure. The AlN and composite AlN/Al2O3 coatings had a crystalline structure with a surface morphology and structure of the fracture cross-section typical for the crystalline phase (figure 2.). The changes observed of the coatings’ structure corresponded to the changes in the mechanical properties.

The mechanical properties of the coatings are the hardness $H$ and the effective Young's modulus $E^*$. The mechanical behavior of the films is characterized by the ratio $H/E^*$[10, 11]. This ratio is proportional to the fracture toughness of the film and the resistance of the material to plastic deformation. Films with lower values of the effective Young's modulus in general have enhanced resistance to cracking and plastic deformation. It is well known that there is a strong correlation between the mechanical properties and the coating structure. For example, incorporating a nano-crystalline phase transition layer of a composite coating in the amorphous matrix strongly increases the values of $H$ and $H/E^*$ and the mechanical properties of the nitride/oxide composite films. The mechanical parameters of Al2O3, AlN and composite nitride/oxide AlN/Al2O3 coatings deposited on stainless steel (SS) and Ti alloy substrates are presented in table 1.

### Table 1. Mechanical characteristics of composite coatings deposited on SS and Ti alloy substrates.

| Material/Coating type   | Mechanical parameters (average results 10 tests) | Mechanical Behavior |
|-------------------------|--------------------------------------------------|---------------------|
|                         | Hardness $H$ [GPa] | Young’s Modulus [GPa] | $H/E^*$ | Adhesion [N] |
| SS/ Al2O3              | 9.7 | 174.7 | 0.057 | 43.1 |
| SS/ AlN                | 14.3 | 184.4 | 0.078 | 50.3 |
| SS/ AlN/ Al2O3         | 12.9 | 178.6 | 0.071 | 45.9 |
| Ti/ Al2O3              | 9.2 | 170.3 | 0.052 | 37.1 |
| Ti/ AlN                | 13.8 | 183.1 | 0.075 | 47.2 |
| Ti/ AlN/ Al2O3         | 12.5 | 177.9 | 0.069 | 40.7 |
The total abrasive wear of composite ceramic coatings subjected to abrasion by various materials (diamond, corundum and SiC particles) is presented in figure 3. The composite coatings deposited on stainless steel and titanium alloy substrates demonstrated an increased wear resistance in comparison with the uncoated substrates and the single oxide and nitride layers.

The addition of a nitride layer to the composite coatings’ structure strongly increased the films hardness (from 9 GPa to 14 GPa) and changed the $H/E^*$ ratio from 0.05 to 0.08. The incorporation of the nano-crystalline phase in the amorphous matrix strongly improved the nitride/oxide composite coatings’ mechanical properties. The enhancement of mechanical properties, such as hardness, toughness, elastic recovery and wear resistance of nitride/oxide composite coatings may prove to be of considerable importance for many tribological applications.

4. Conclusions
The results reported in the paper demonstrate an improvement of the tribological characteristics of metal bearing surfaces upon covering by ceramic coatings. The wear resistance, hardness and toughness parameters increase in the case of composite nitride/oxide AlN/Al$_2$O$_3$ coatings. The deposition of a ceramic coating on metal substrates (stainless steel 1H18N9, titanium alloy Ti$_6$Al$_4$V) allows one to combine the ceramic materials’ inertness with the hardness and failure strength of the supporting metals, which is of paramount importance for the next generation of bearing surfaces. The incorporation of a nano crystalline phase in the amorphous matrix strongly increases the mechanical properties of the nitride/oxide composite films. The application of ceramic coatings on metallic materials represents an effective alternative to ball bearing manufacturing.

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