УДК 616-089.843(045)

The improvement of tribological parameters of nano structural multilayer coatings for unipolar modular joint applications

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Key words: hemiarthroplasty, implant materials, nano structural multilayer coatings, tribological performance, biocompatibility

Femoral neck fractures are a common insufficiency fracture in the elderly. The application of ceramic coatings on metallic materials represents an effective way to formation of advanced surfaces of unipolar and bipolar modular prosthesis for joint arthroplasty. The enhancement of mechanical properties such as hardness parameters up to 14 GPa, adhesion strength up to 50 N and low friction coefficient of multilayer coatings, with strong tendency to decrease in fluids (0.07), effective Young's modulus, toughness, elastic recovery and wear resistance of the coatings is very important for tribological performance of the next generation of ceramic coated modular prosthesis. The joint femoral head surfaces with nano structural multilayer coatings demonstrate improved biocompatibility due to wettability increasing and fluid friction characteristics advancing.

Переломы шейки бедренной кости наиболее часто встречаются у людей пожилого возраста. Нанесение керамических покрытий на металлические материалы является эффективным способом усовершенствования поверхностей униполярных и биполярных модульных протезов для артропластики суставов. Повышение механических свойств покрытий эндопротезов (износостойкости, пластичности, твердости до 14 ГПа, адгезионной прочности до 50 Н), а также низкие значения модуля Юнга и коэффициента трения в жидкостях организма (до 0,07) очень важны для улучшения трибологических параметров нового поколения модульных эндопротезов с керамическими покрытиями. Показана повышенная биосовместимость бедренного компонента эндопротеза, а именно головки с наноструктурным многослойным покрытием, благодаря увеличению смачиваемости поверхности и уменьшению жидкостного трения.

Introduction

At the process of the femoral head arthroplasty the most important is the evaluation of patient's anatomical features for enhancement of tribological parameters of modular joints. The principal advantage of modular prosthesis application is the possibility of revision operation in the case of significant migration of joint femoral head to pelvis.

Ravikumar [1] followed 290 patients with displaced subcapital femur fractures for 13 years and reported that a higher rate of revision surgery was needed in those who underwent open reduction (as compared to those who had hemiarthroplasty or total hip arthroplasty), due to internal fixation nonunion and avascular necrosis. Similarly, in a study of 222 patients reported by Frihagen [2], hip hemiarthroplasty was associated with

better functional outcomes than internal fixation in the treatment of displaced fractures of the femoral neck in elderly patients. After adjusting for confounding factors such as differences in the level of function before injury between the groups, the degree of return to the preinjury state was significantly greater ($p = 0.04$) when using the unipolar prosthesis. Thus, it seems that femoral head replacement surgery is preferred in the elderly [3–8].

The total and modular replacement of hip-femoral joints is one of the most successful and effective surgery operations in modern medicine practice [9, 10]. The long-term experience of different patience group investigations demonstrates high survival parameters under medical observations above 20–30 years. The serious problem is arising of cyclic mechanical loads of prosthesis coupling and friction elements accelerated destruction due to the patient's motion activity [11, 12]. There is the direct effect of wearing rate of artificial joint on the next osteolysis processes, aseptic loosing and revision operations needs.

Recently the main directions of joint's tribological parameters improvement are the advancing of existed joint sliding coupling characteristics (metal-metal, metal-ceramic, ceramic-ceramic couples) and search for alternative materials (metal, ceramic, coatings) [13–15]. Ceramics are chemically resistant and can be used in wet environments where steel bearings would rust. In many cases electrically insulating properties of ceramic materials may also be valuable in bearings. The ceramic materials using allows to improve the joint wettability characteristics and fluid friction conditions [16]. The ceramic materials possess high hardness and wear resistance parameters, biocompatibility in comparison with metal elements but there is the risk of brittle failure of ceramic heads [17, 18]. The negative results of metal and ceramic materials application are accumulation of toxic wear debris in the surrounded implant tissues and next dissemination of wear particles to the internal organs: liver, spleen, kidneys [19–21]. The application of metal materials with ceramic coatings is the effective way of alternative bearing surfaces formation. The ceramic aluminum nitride AlN, aluminum oxide Al_2O_3 and nano composite oxynitride coatings are widely used as protective coatings against wear, diffusion and corrosion [22–24]. The enhancement of mechanical properties such as hardness parameters, effective Young's modulus, and toughness of the coatings is very important for tribological performance of the next generation of ceramic-coated femoral heads of modular and total joints.

The aim of the study was the mechanical parameters advancing of unipolar modular joint prosthesis with femoral head coated by mono and bilayer ceramic films for patients of elder age groups with a femoral neck fractures.

Materials and Methods

The substrates were the most popular load-bearing materials such as titanium-based alloy Ti (Ti4Al6V) and SS stainless steel samples (1H18N9). The aluminum oxide Al_2O_3, aluminum nitride AlN and composite nitride/oxide AlN/Al_2O_3 coating deposition was performed in high vacuum pumping system with the base pressure about 10^{-3} Pa. The magnetron discharge power was 1–4 kW, power of activated oxygen source up to 1 kW, Ar pressure $p_{Ar} = 1{,}8 \cdot 10^{-1}$ Pa, oxygen flux $q = 30$ cm^3/min, nitrogen flux $q = 23{,}5$ cm^3/min, magnetron voltage $U_m = 570$ V, magnetron current $I_m = 8$ A, total pressure $p = 2{,}2 \cdot 10^{-1}$ Pa, coating deposition rate 8 μm/hour. The ion source was applied for etching and cleaning the surface of samples before deposition process for composite coatings synthesis performance.

The sputtering process was made in the regimes far from the target passivation mode for next nitride/oxide coatings deposition with highly stoichiometric composition. Also, such deposition conditions allow to avoid micro-arcs and micro-drops formation increasing the wear resistance properties.

Fig. 1 presents the current-voltage characteristic of the magnetron with targets of aluminum in a mixture of argon with oxygen or nitrogen at various reactive gas flows. The optimum conditions were realized for the upper part of current voltage curves of magnetron discharge in argon for both oxygen and nitrogen gases.

The structure of monolayer and multilayer magnetron sputtering thin films was investigated by means of photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) methods. X-ray diffraction profiles of as-deposited coatings demonstrate a lower crystallinity. The structural analysis of coatings by means of XPS method also was made [25]. The photoelectron spectra of Al2p, O1s, N1s and C1s were observed and confirmed strong compound stoichiometric composition.

The coatings adhesion properties, hardness and elastic modulus, were evaluated by standard methods with the use of Revetest (CSM Instrumets) and the Rockwell indenter with the tip radius 200 μm, within the load range 200 N.

The mechanical properties of the coatings are the hardness H and effective Young's modulus E*. Mechanical behavior of the films is characterized by the ratio H/E*[28–30]. The ratio is proportional to the fracture toughness of the film and to the resistance of the material to plastic deformation. It means that the films with enhanced resistance to cracking and plastic

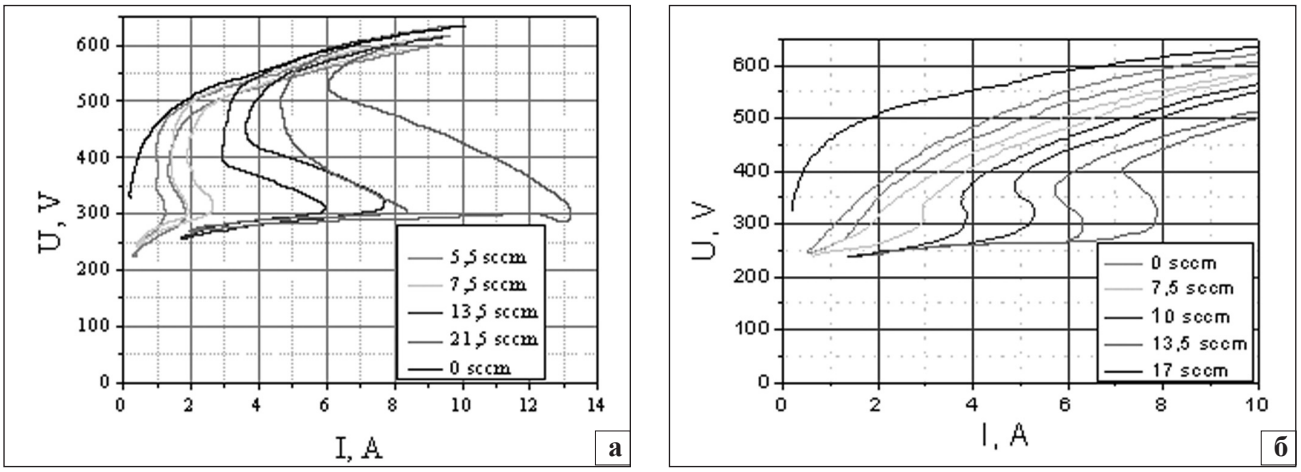

Fig. 1. Current voltage characteristics of magnetron discharge for different flows of oxygen (a) and nitrogen (b), argon pressure $p = 1.8 \cdot 10^{-1}$ Pa

deformation should have lower values of effective Young's modulus.

The friction coefficient of mono and multilayer coatings was about 0.1 was less than for metal materials and nitride coatings and has strong tendency to decrease in fluids (0.07).

Advancing contact angles were measured by Wilhelm's method (Kruss K12) at temperature 20 °C [25].

The coating surface structure and morphology were estimated by means of scanning electron microscopy (SEM) (JEM 2100) and atomic force microscopy (AFM) (Quesant Instrument Corporation, USA) methods.

For wear resistance testing the abrasion tests was performed on a CAT-S-AE (CSM Instrumets) microscale abrasion tester. The ball was a micro-blasted 25 mm diameter hardened steel sphere (SAE 52100, 61 ± 2 HRC, Ra = 2.5 ± 0.3 μm) and abrasive slurry was a suspension of diamond particles (mean size 2–4 μm). The ball rotational speed was set to provide a linear velocity of 0.1 m/s in all tests. The total abrasive wear of composite ceramic coatings at abrasion action conditions was estimated according to methods [26, 27].

The analysis of hemiarthroplasty results of 26 patients (woman, age 72–86 years old) was made. The average age was 76 years old. For prosthesis fixation, the Harding interior approach was performed. The stem of joint was fixated by cement. For 14 patients the modular prosthesis made of stainless steel with femoral head coated by ceramic films were implanted. For 12 patients the standard Austin- Moore prosthesis made of stainless steel without coated surfaces were used.

The average terms of inpatient treatment after hemiarthroplasty of hip-femoral joint were about 14 days. After 3 days of post operation treatment the patients were permitted to walk with go-cart and graduated weight bearing on the operated extremities. The radiographic data of femoral joint in frontal view were observed after 3, 6 and 12 months of postoperative period.

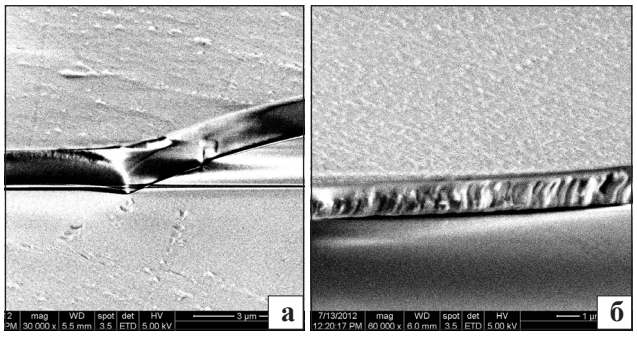

Fig. 2. The SEM micrographs of fracture section of Al2O3 (a) and AlN (b) films

Results and Discussion

The XPS results demonstrate the strong Al2O3 oxide stoichiometric composition of deposited coatings. The nano structural surface parameters were observed by SEM and AFM methods. The surface of oxide Al2O3 coatings has smooth relief with uniform cross-section structure. The AlN coatings have crystalline structure with crystalline phase fracture section (fig. 2.) and composite films structure AlN/Al2O3 were formed (fig. 3). There is the correlation between the mechanical properties and coating structure. The incorporation of the nano crystalline phase transition layer of composite coating in the amorphous matrix strongly increases the values of H, H/E* and mechanical properties of nitride/oxide composite films. The research of tribological parameters of oxide coatings deposited on load-bearing substrates such as 1H18N9T and Ti6Al4V were made.

The mechanical characteristics of Al2O3, AlN and composite nitride/oxide AlN/Al2O3 coatings deposited on the SS and Ti alloy substrates were presented in the table.

Table

Mechanical characteristics of composite coatings deposited on the SS and Ti alloy substrates

Material/Coating type	Mechanical parameters (average results 10 tests)			
	Hardness H [GPa]	Young Modulus [GPa]	H/E*	Adhesion [N]
SS/ Al_2O_3	9.7	174.7	0.057	43.1
SS/ AlN	14.3	184.4	0.078	50.3
SS/ AlN/ Al_2O_3	12.9	178.6	0.071	45.9
Ti/ Al_2O_3	9.2	170.3	0.052	37.1
Ti/ AlN	13.8	183.1	0.075	47.2
Ti/ AlN/ Al_2O_3	12.5	177.9	0.069	40.7

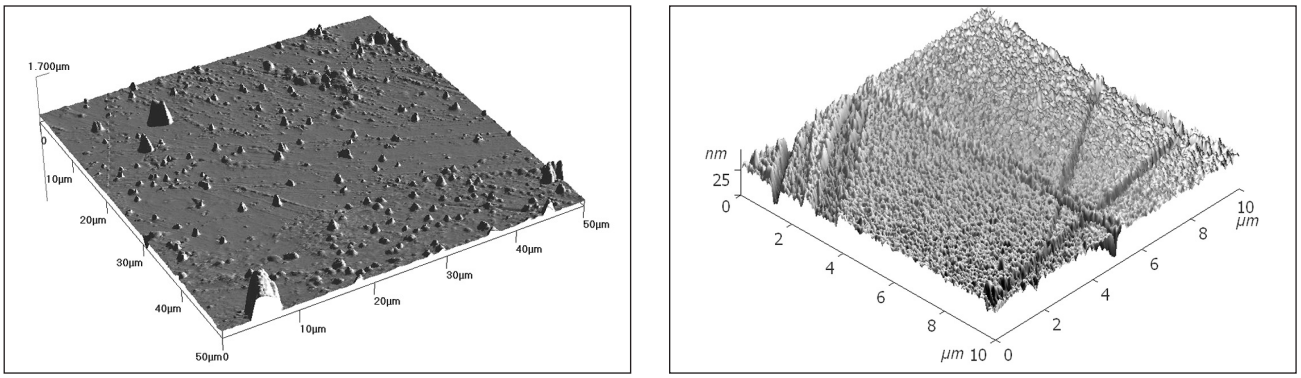

Fig. 3. Surface structure of the deposited oxide Al2O3 (a) and composite AlN/Al2O3 (b) coatings by AFM method

The total abrasive wear of composite ceramic coatings at abrasion action conditions was presented (fig. 4). The composite coatings deposited on Ti alloy substrates demonstrate the increasing of wear resistance in comparison with uncoated substrate and mono layer both oxide and nitride coatings. The character of abrasive effect on coating's structure was analyzed by micrographs (fig. 5).

The addition of nitride layer in the composite coating's structure strongly increases the hardness of films from 9 GPa to 14 GPa and the ratio H/E* from 0.05 to 0.08. The enhancement of mechanical properties such as hardness, toughness, elastic recovery and wear resistance of nitride/oxide composite coatings is very important for many tribological applications.

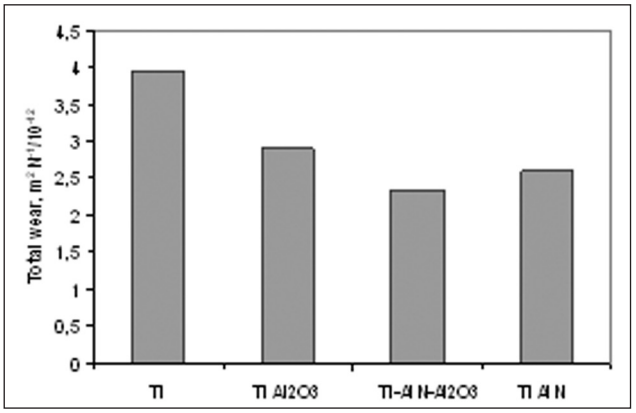

Fig. 4. The total surface abrasive wear of Al_2O_3, AlN and AlN/Al_2O_3 composite coatings deposited on Ti alloy substrates

The hardness parameters, toughness and wear resistance were increased in the case of composite nitride/oxide AlN/Al_2O_3 coatings. The high hardness parameters up to 14 GPa, adhesion strength up to 50N and low friction coefficient of oxide coatings, with strong tendency to decrease in fluids (0.07) were obtained. The hydrophilic nature of coated surfaces in comparison with metal one was demonstrated.

The analysis of clinical results of 26 patients (woman, age 72–86 years old) was presented. Patient's group

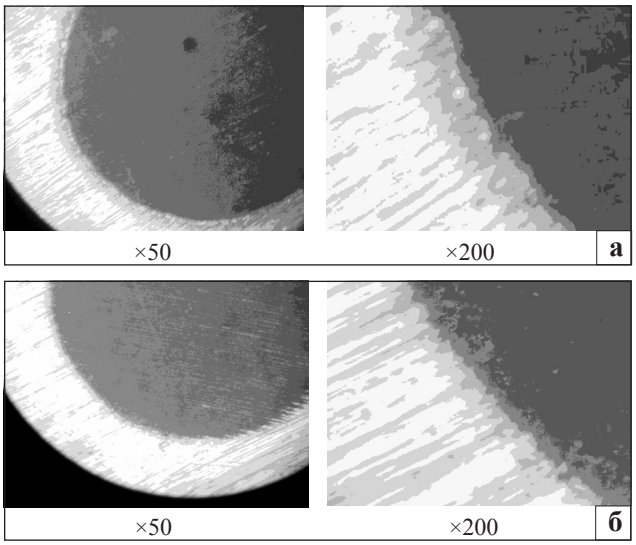

Fig. 5. The micrographs of abrasive wear damage (top view of the wear crater) of AlN/Al_2O_3 (a) and Al_2O_3 (b) ceramic coatings deposited on Ti alloy substrates by optical microscope (magnification ×50, ×200)

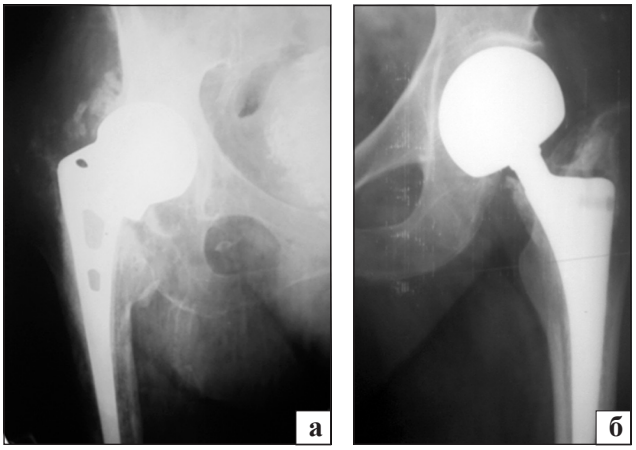

Fig. 6. Radiographs of clinic application of modular femoral joints: a) without ceramic coatings (Austin-Moore prosthesis, femoral head migration was up to 6 mm after 2 years under medical observation); b) with multilayer coatings (migration of the femoral head coated by ceramic films was in the range 1.5–2 mm after 2 years postoperative observation)

with femoral heads coated by oxide and oxide/nitride layers ofmodular prosthesis has greater range of motion in the operated joint in comparison with the standard Austin-Moore prosthesis patient's group ($P \leq 0,05$).

The significant differences in the femoral head replacement were observed (fig. 6). For 12 patients with the standard Austin- Moore prosthesis the femoral heads migration was 2–6 mm after 2 years under medical observation. The migration of the femoral heads coated by ceramic films for 14 patients with the modular prosthesis was in the range 1.5–3 mm after 2 years postoperative observation.

Conclusions

The results demonstrate the improvement of tribological characteristics of metal bearing surfaces coated by ceramic coatings. The observed changes of the coating's structure result in some mechanical properties changes.

The mono and multilayer ceramic-coated femoral heads of unipolar joints have some principal advantages in comparison with uncoated femoral heads. The hydrophilic surface properties and low friction coefficient increase the joint lubrication by synovial joint fluid in the coupling process with natural cartilage and high tribological parameters decrease the wear debris accumulation and inflammatory complications in the contact zone.

The stainless steel and titanium alloy modular and total joints with ceramic mono and multilayer coatings exhibited the best biocompatibility due to fluid friction characteristics advancing and absence of inflammatory reactions on the joint-cartilage interface in comparison with uncoated samples. The clinical approbation of the modular joints with ceramic-coated femoral heads allows to suggest principally new strategies for femoral neck fractures treatment which are the most insufficiency fracture in the elderly.

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The article entered release 29.01.2014

УСОВЕРШЕНСТВОВАНИЕ ТРИБОЛОГИЧЕСКИХ ХАРАКТЕРИСТИК НАНОСТРУКТУРНЫХ МНОГОСЛОЙНЫХ ПОКРЫТИЙ ПРИ ПРИМЕНЕНИИ УНИПОЛЯРНЫХ МОДУЛЬНЫХ ЭНДОПРОТЕЗОВ СУСТАВОВ

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