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Boron nitride/titanium nitride laminar lubricating coating deposited by pulsed laser ablation on polymer surface

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Abstract. Pulsed laser deposition technique was applied for covering elastic cast-polyurethane membranes with titanium nitride and boron nitride layers. The deposition process was realized using a Nd:YAG laser with Qswitch in stages; firstly the membranes were coated with ultra-thin titanium nitride layer (Ti_xN) by evaporation of a metallic titanium disk in nitrogen gas atmosphere and then a layer of boron nitride (BN) was deposited by ablation of hexagonal h-BN target in argon atmosphere. The surface morphology was observed by scanning electron microscopy. Chemical composition was analyzed by energy dispersive X-ray spectrometry. The phase analysis was performed by means of grazing incidence X-ray diffraction and attenuated total reflection infrared spectroscopy. The crystallographic texture was measured. The wear test was performed by pin-on-disk method. Hexagonal boron nitride layers with (0001)[uvtw] texture with flake-like grains were fabricated. The structure and texture of boron nitride was identical irrespectively of substrate roughness or BN thickness. Pin-on-disk wear tests showed that the coatings effectively decreased the friction coefficient from two to even four times comparing to pure polyurethane and polyurethane covered with graphite. This proved that deposited layers can replace graphite as a lubricating material used to protect polymer surfaces.

Key words: hexagonal boron nitride, lubricating coating, pulsed laser deposition.

1. Introduction

A polymer surface needs to be protected against wear when used in strong deformation or friction conditions. Boron nitride (BN) is an excellent lubricant [1–3] while titanium nitride (TiN) is successfully used for biocompatible protective layers [4]. Both materials are non-toxic and safe for human body what makes them suitable for biomedical applications [1, 2]. Boron nitride is a man-made compound which has structure similar to carbon allotropes. It exists in soft structures i.e. hexagonal h-BN, rhombohedral r-BN and semi-crystalline turbostratic t-BN which all have laminar graphite-like structure. All these forms of BN are known as insulating solid lubricants with very low thermal expansion coefficient. They are characterized by excellent chemical inertness, oxidation stability and corrosion resistance [1–3, 5].

Combination of TiN and BN into one single laminar coating may result in obtaining of a very good tribological composite. In this article two-layers system was presented. It consisted of a titanium nitride film, thin enough not to be brittle, and a much thicker lubricating layer of boron nitride. This coating was proposed as a supplement of mechanically embedded graphite for covering polyurethane membranes used in pump applied in an artificial heart.

Polymers may easily degrade if heated above hundreds Celsius degrees, therefore for coverage, the pulsed laser deposition technique (PLD) was chosen. On the contrary to other physical vapour deposition (PVD) methods, the PLD does not require substrate heating and allows producing high quality thin films on unheated surface. In this method the laser beam is focused on a target's surface which leads to ablation of its upper layer. The evaporated material undergoes in the state of plasma consisting of ions, atoms and clusters and is deposited on a substrate forming a thin film [6–9].

2. Experimental part

The pulsed laser deposition technique was applied for covering elastic membranes made from cast-polyurethane both with titanium nitride and boron nitride layers. The process was realized in Joanneum Research Laser Centre Leoben in Austria. Nd:YAG laser with Q-switch operating in a pulse mode (with wavelength $\lambda = 1064$ nm, output beam energy E = 0.6 J, pulse duration $\tau = 10$ ns and frequency f = 10 Hz) was used. The radiation beam was directed to the target surface at an angle of 60°. Deposition was performed without the substrates heating. The gas flow rate inside the chamber was hold at 30 sccm. Polyurethane membranes with thickness from 0.27 to 0.50 mm and diameter of 50 mm were applied as substrates. The substrates with smooth surface were denoted as PU while the rough ones were marked as PUAR (Table 1).

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Table 1
Samples description

Name of the sample	Estimated thickness of boron nitride	Polyurethane substrate
BN/Ti_xN/PU4	200 nm	smooth
BN/Ti_xN/PU5	400 nm	smooth
BN/Ti_xN/PUAR7	400 nm	rough

Elastomer membranes were delivered by the Foundation of Cardiac Surgery Development in Zabrze in Poland. The deposition process was realized as follows. First the membranes were coated with ultra-thin titanium nitride layer (Ti_xN) by evaporation of metallic titanium disk in nitrogen atmosphere. Then layer of boron nitride (BN) was deposited by ablation of hexagonal h-BN target in argon gas atmosphere (Fig. 1). BN material used for target preparation was bought in Johnson Matthey Company. On the basis of number of laser pulses it was estimated that foreseen thickness of titanium nitride was around 10 nm while in the case of boron nitride 200 nm or 400 nm, depending on sample (Table 1). Due to very low thickness of titanium nitride identification of its stoichiometry was impossible and therefore “x” index was used in its formula (Ti_xN). The surface morphology was observed by a Scanning Electron Microscopy (SEM) technique applying a Philips XL30 and FEI XL30 E-SEM microscopes. Chemical composition was analyzed by an Energy Dispersive X-ray Spectrometry (EDX) using EDX Link ISIS and EDAX Genesis 4000 spectrometers. The phase analysis was performed by means of Grazing Incidence X-ray Diffraction (GIXRD) applying Bruker D8 Discover (operating with Cu radiation) and Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) using Bruker Hyperion + Tensor 37 spectrometers. The crystallographic texture was measured by a X-ray goniometer Philips PW3020 + ATC-3 (operating with Co radiation). Pole figures were constructed in LaboTex program. The wear test was performed by the pin-on-disk method using a CSM Instruments Micro-Combi-Tester. In this test two samples with identically deposited layers were touched face to face and moved in reciprocating movement in 500 cycles along 2 mm path under load of 0.05 MPa or 0.20–0.25 MPa.

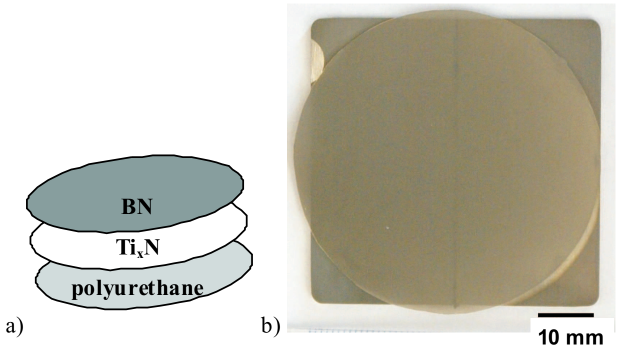

Fig. 1. Scheme of BN/Ti_xN coating deposited on the polyurethane membrane (a) and photo of the surface of BN/Ti_xN/polyurethane specimen (b)

3. Results and discussion

3.1. Phase composition. X-ray diffractograms exhibited a characteristic 0002 reflection of h-BN phase. The peak was seen independently on thickness of deposited boron nitride and roughness of polyurethane substrate (Fig. 2). Other reflections might be not visible because of very low thickness of BN and/or its strong crystallographic texture. Interplanar distance determined on the basis of 0002 peak position was 0.333 ± 0.002 nm which was in a perfect agreement with h-BN XRD reference pattern (ICDD No. 34-0421). It revealed that pure hexagonal boron nitride was obtained. Large band visible around 15–25°2Θ (Fig. 2) was a signal of polyurethane. Due to ultra-low thickness of titanium nitride any signals of Ti_xN were visible in X-ray diffractograms. Presence of hexagonal boron nitride was confirmed by ATR-IR spectra having absorption bands with maximum at around 1365 and 788–786 cm^{-1} which were characteristic wavelength for h-BN phase (Fig. 3).

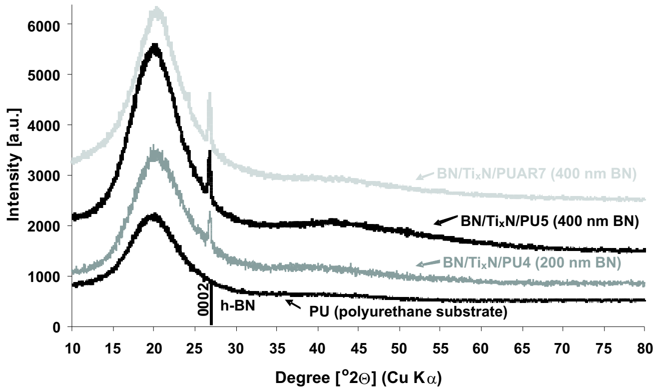

Fig. 2. X-ray diffractograms of polyurethane membrane before deposition (PU) and polyurethane membrane with BN/Ti_xN layers

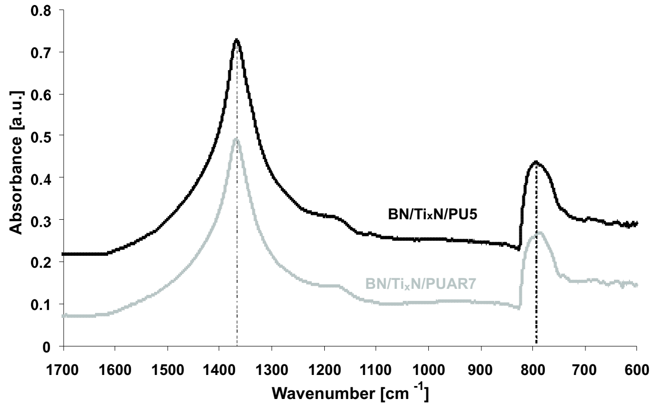

Fig. 3. ATR-IR spectra of BN/Ti_xN layers deposited on polyurethane membranes (smooth PU5 and rough PUAR7)

3.2. Texture. The texture analysis showed that h-BN crystallites were oriented with their basal planes 0001 parallel to the polymer surface revealing strong (0001)[uvtw] orientation (Figs. 4, 5). Similar texture was stated independently on h-BN thickness and polymer substrate roughness. The difference in

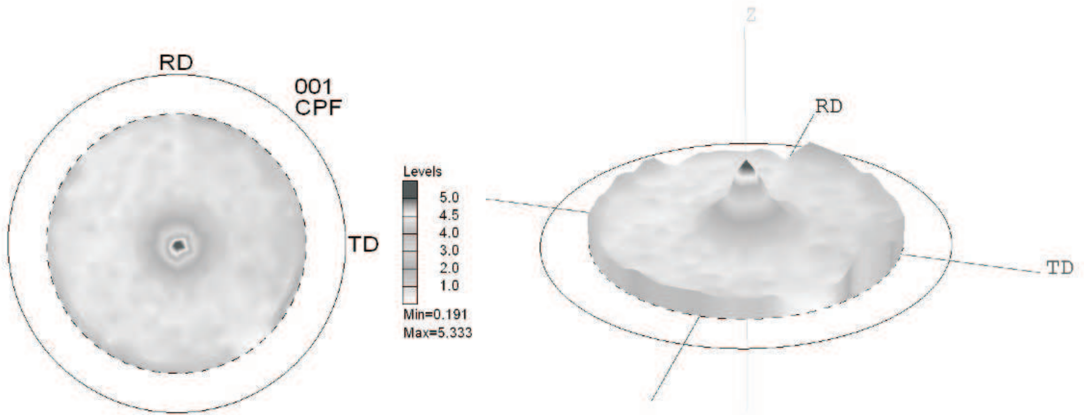

Fig. 4. Pole figure of 0001 h-BN in 400 nm layer of BN deposited on rough polyurethane covered earlier with Ti_xN

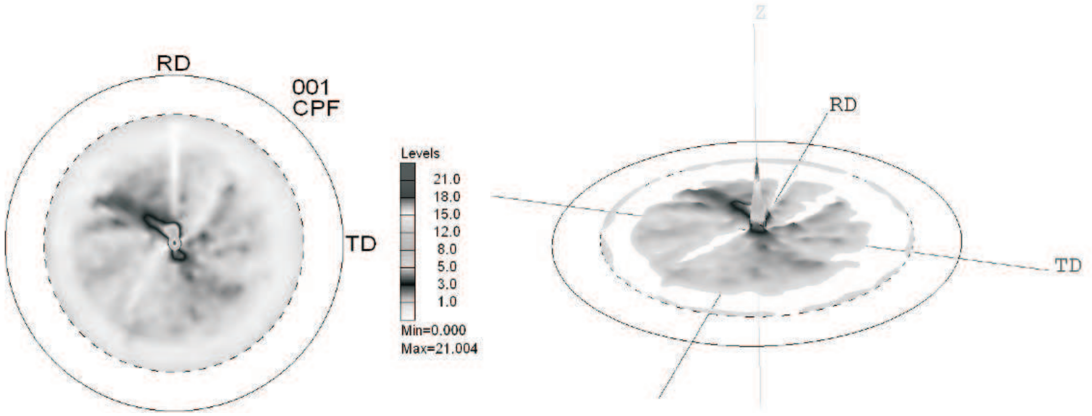

Fig. 5. Pole figure of 0001 h-BN in 400 nm layer of BN deposited on smooth polyurethane covered earlier with Ti_xN

the texture index (Figs. 4, 5) is due to various counting time during the X-ray measurements. This type of h-BN orientation was characteristic for the layers obtained without substrate bias and strong ion bombardment [8–10].

3.3. Surface morphology and chemical composition. The observations performed by SEM showed that the h-BN layers were composed of flake-like grains (Fig. 6a). The same morphology had been previously observed in boron nitride deposited by Nd:YAG-based PLD system on steel covered with titanium [8, 9]. Morphology and thickness of BN (measured using a mechanical profilometer) were homogenous along each sample proving capability of Nd:YAG-based PLD system for covering samples with area so large as 2500 mm^2. Boron nitride had poor adhesion to titanium nitride interlayer and could be easily removed while titanium nitride was very adherent to polyurethane substrate. EDX spectra showed the presence of B, C, N, O, Ti elements in BN/Ti_xN/polyurethane samples (Fig. 7). Boron, nitrogen, carbon and oxygen signals came from BN, Ti_xN and polyurethane. Titanium signal confirmed Ti_xN presence.

3.4. Wear test. The wear test was performed using samples with the largest boron nitride thickness i.e. 400 nm. For comparison the same wear test was performed using uncovered polyurethane membranes as well as membranes with mechanically embedded graphite powder. On the basis of an intensity of boron EDX signal, which only came from BN, the amount of removed h-BN was evaluated. After test performed at load of 0.05 Mpa there was no detectable remove of h-BN in the case of layers obtained both on smooth and on rough substrate. In the case of test load of 0.20–0.25 MPa 15% of BN deposited on smooth and 17–39% deposited on rough polymer substrate was rubbed off (Table 2). Variability observed in the latter case (BN/Ti_xN/PUAR7 specimen) was connected with the fact that more material was removed from the top of asperities than from valleys of rough sample. After the wear test performed at loading of 0.05 MPa the morphology of BN layer (Fig. 6b) was quite similar to the one observed before the test (Fig. 6a) while in the case of higher load of 0.20–0.25 MPa a distinct flattening of the h-BN flakes was observed (Fig. 6c). The friction coefficient measurements showed large improvement of lubricating properties of polymer covered with the BN/Ti_xN coating (Figs. 8, 9). Fluctuations visible (Figs. 8, 9) after every 100 cycles were connected with the applied test procedure. During the tests after each 100 cycles, samples were unloaded, separated and optical microscopy investigations were done. Afterwards samples were joined and loaded again and the test was continued. During the tests at lower load (Fig. 8) the friction coefficient for pure polyurethane noted at the end of test was $\mu = 0.8$. Presently used mechanically embedded graphite resulted in $\mu = 0.45$. The application of BN/Ti$_x$N coating allowed to reducing the friction coefficient up to $\mu = 0.15$–0.2. At the end of the tests performed at loading of 0.20–0.25 MPa the friction coefficient of pure polyurethane was around $\mu = 0.75$ while the one with graphite layer $\mu = 0.9$ and with BN/Ti$_x$N layers equalled to $\mu = 0.3$–0.4 (Fig. 9). The course of dependence of the friction coefficient was smoother in samples with BN/Ti$_x$N coating comparing to uncoated polyurethane. Beneficial properties of the obtained BN/Ti$_x$N coating were connected with hexagonal structure of boron nitride and its favourable texture with (0001) slip plane placed in the direction of sliding. PLD allowed for formation of BN/Ti$_x$N films on polyurethane which effectively decreased friction from two to even four times comparing to pure polyurethane and polyurethane covered with graphite.

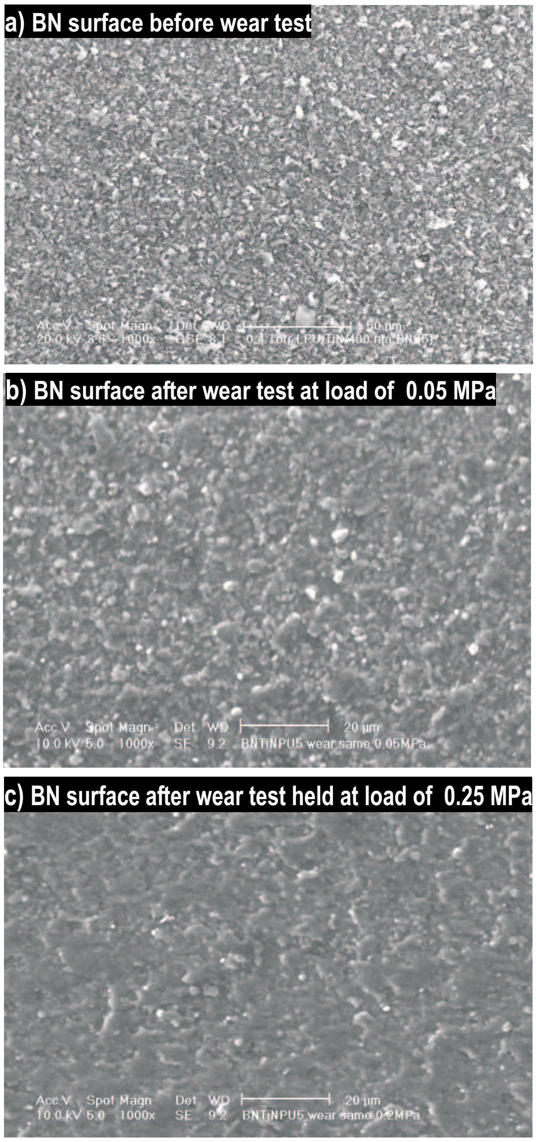

Fig. 6. Surface morphology (SEM images) of boron nitride layer in BN/Ti$_x$N/PU5 sample before (a) and after (b, c) wear test

Table 2
Relative amount of boron nitride removed during wear test at load of 0.20–0.25 MPa

Sample	Relative amount of removed boron nitride
BN/Ti$_x$N/PU5 (on smooth polyurethane substrate)	15%
BN/Ti$_x$N/PUAR7 (on rough polyurethane substrate)	39%
BN/Ti$_x$N/PUAR7 (on rough polyurethane substrate)	17%

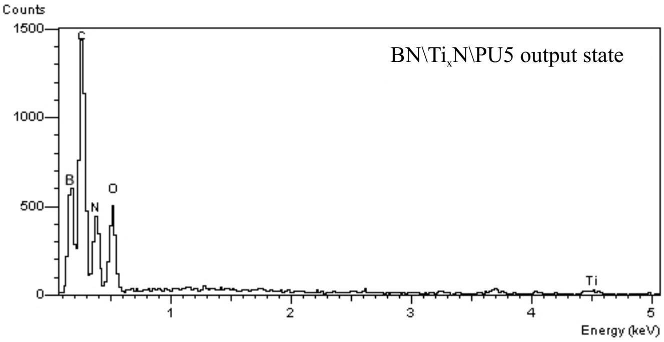

Fig. 7. EDX spectrum of BN/Ti$_x$N/PU5 specimen

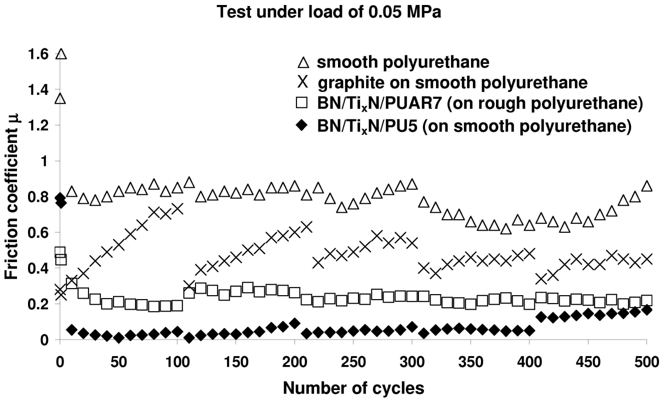

Fig. 8. Dependence of the friction coefficient on number of cycles during wear test performed under load of 0.05 MPa

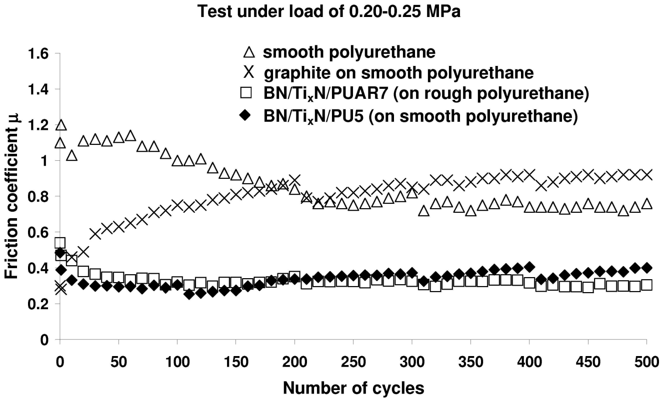

Fig. 9. Dependence of the friction coefficient on number of cycles during wear test performed under load of 0.20–0.25 MPa

4. Conclusions

The pulsed laser deposition performed using a Nd:YAG laser allowed for obtaining lubricating coatings composed of the boron nitride and the titanium nitride on thin elastic polyurethane membranes. Hexagonal boron nitride with (0001)[uvtw] texture with flake-like grains was fabricated. The structure and texture of the h-BN was identical irrespectively of the substrate roughness or boron nitride thickness. The pin-on-disk wear tests showed that BN/Ti_xN layers effectively decreased the friction coefficient from two to even four times comparing to pure polyurethane and polyurethane covered with graphite. BN/Ti_xN layers can successfully replace graphite coating as a lubricant to protect polymer surfaces.

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