STRUCTURAL AND MECHANICAL PROPERTIES OF BORON NITRIDE THIN FILMS DEPOSITED ON STEEL SUBSTRATES BY PULSED LASER DEPOSITION

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Abstract

The article presents preliminary results of investigation on structure, morphology and mechanical properties of boron nitride thin films prepared by pulsed laser deposition on various steel substrates. In order to improve adhesion and reduce internal stresses, substrates were subjected to gas nitriding. To increase gas ionization in the chamber and provide the deposited particles with higher energy RF discharge generator was used. Structure and morphology of coatings were examined by atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). Mechanical properties like nanohardness (sclerometric) and elastic modulus (using approach curves) were characterized by UNMT. Adhesion of coatings was measured by scratch tests; critical load was determined on the basis of microscopic observation and friction force and acoustic emission runs. On the basis of obtained results, possibility of using steel as substrate for BN thin films deposition was confirmed. Stable, crystalline, multiphase coatings with good adhesion to the steel substrate were obtained. It was also proved that mechanical properties of prepared coatings and their adhesion to the substrates strongly depend on the type of the substrate. In the next stage tribological properties of BN, coatings will be examined in particular in terms of wear resistance and friction coefficient between coatings and steel.

Keywords: *boron nitride, pulsed laser deposition, nanohardness, elastic modulus, critical load*

1. Introduction

Thin films forming a group of composite materials are becoming more widely used in optics, electronics and construction of machines. The main tasks of lubricating coatings are improvement of mechanical properties (hardness, elastic modulus), raise of corrosion resistance and, above all, reduction of friction and wear of [2]. One of the most promising materials for that purpose, which fulfil all mentioned requirements, is boron nitride (BN). Boron nitride is inorganic chemical compound, consisting of the same number of boron and nitrogen atoms and is isostructural and isoelectronic with carbon. Analogous to carbon, BN forms both hard, diamond-like sp^3-bonded phases and softer, graphite-like sp^2-bonded phases. The most common and stable phases are soft hexagonal boron nitride hBN and hard cubic boron nitride cBN [7]. All phases of boron nitride have a number of common properties like high thermal and chemical stability, high corrosion resistance, no solubility in water and most common acids. Unlike diamond, BN phases does not react with ferrous metals below the temperature of 1500°C. At the same time, there are significant differences between phases with sp^2 and sp^3 hybridization. Sp^2 phases, like hBN, rBN are very soft and posses lubricating abilities similar to graphite [8]. Hexagonal boron nitride has good lubricating properties both in low and high temperatures (up to 900°C, even in presence of oxidizing atmosphere). Due to its structure (strong bonds within the layer, weak between layers) hBN shows anisotropic properties, such as in case of conductivity and thermal expansion. Cubic phase, due to covalence-ionic nature of chemical bonds, has very high hardness (second only to diamond). It is characterized by low friction coefficient and high wear resistance. In addition, the layered nanocomposites composed of hard cBN and soft hBN phases with good lubricating abilities are ideal for covering surfaces of bearings. Wurtzitic boron nitride (wBN) with hardness similar to cBN, has lower thermodynamic stability and the tendency to transform to stable hBN phase.

In the vast majority of cases, BN coatings are deposited on silicon substrate, due to the fact that the highest content of cBN phase was observed on hard, covalence substrates like Si, SiC, diamond, sintered carbides [3,4]. Thin BN films deposited on soft metals (Al, Ag) show significantly lower content of cubic phase than those deposited on hard metallic substrates (Nb, Ta, Ni) [1]. The authors of many publications point to significant difficulties in obtaining hard coatings with good adhesion deposited directly on steel; few papers describe the possibility of deposition of stable, hard or soft phases of boron nitride on high-speed, bearing or stainless steels with very good tribological properties [5,6]. A small number of domestic and foreign publication that focus on investigation on mechanical and tribological properties of BN films deposited on steel substrates led the authors to undertake research and expand current knowledge in that area.

In the article the preliminary results of investigation on structure and morphology of the surface, mechanical properties and adhesion of coatings are presented. Examined coating were deposited by PLD technique on various steel substrates like AISI AMS 6470 nitriding steel (41CrAlMo7), AISI 52100 bearing steel (100Cr6) and AISI M2 high-speed steel (HS6-5-2).

2. Characteristics of investigated materials

In order to improve adhesion and reduce internal stresses, substrates were subjected to gas nitriding, realized in Institute of Precision Mechanics on Nx609 device for regulated gas nitriding. The intension of the process was to produce nitrided layer without the zone of compounds on the surface or with its limited thickness. The parameters of the process of gas nitriding are shown in Table 1.

Tab. 1. Parameters of gas nitriding process

Material	Temperature [^oC]	Time [h]	Atmosphere	Hardness HV0,5
AISI AMS 6470	470	16	$35\%NH_3 – 65\%NH_{3diss}$	1114
AISI 52100	470	16	$35\%NH_3 – 65\%NH_{3diss}$	406
AISI M2	510	1.5	$20\%NH_3 – 80\%N_2$	369

BN thin films were produced by pulsed laser deposition of commercial, pressed hexagonal BN using ArF excimer laser (λ=193nm) in Institute of Optoelectronics, MUT. The stand for coatings deposition, with the scheme of experimental chamber are shown in the Figure 1 and 2.

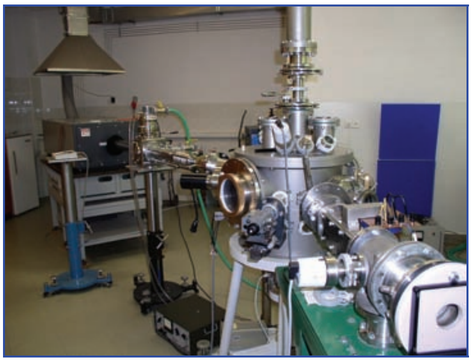

Fig.1. Excimer laser with experimental chamber for thin films deposition (IOE MUT)

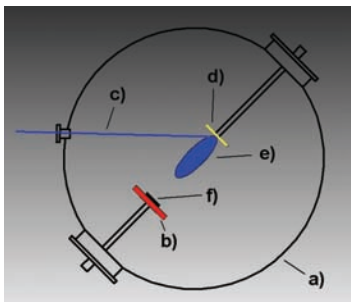

Fig. 2. Scheme of experimental chamber: a) vacuum chamber, b) table with heating, c) laser beam, d) rotating target, e) evaporated material, f) substrate

Before PLD process samples were cleaned by using RF discharge generator (13,56 MHz, 5min/30W and 10min/40W). In order to increase gas ionization in the chamber and provide the deposited particles with higher energy also RF discharge generator (13,56MHz, 30W) was used. The PLD process was carried out with fluence about 1.5-2.3 J/cm^2, the other parameters of PLD process are shown in Table 2.

Tab. 2. Parameters of PLD process

Energy of laser before the chamber and predicted in chamber [mJ]	Repetition [Hz]	Number of shots	Flow rate of nitrogen in chamber [cm^3/min]	Substrate temperature [^{o}C]	pressure [Tor] atmosphere	Deposition time [min]
~220, ~120	5	20000	5	about 500	2,8x10^{-3}, N_2	67

On the basis of the research undertaken on Nanoanalyzer included in UNMT set (Universal Nano & Micro Tester, Center for Tribology Research, USA) and on T8000 Hommeltester profilometer (Hommelwerke, Germany) measured thickness of boron nitride coatings was of the order of 700 nm.

3. Experimental

The main purpose of the study was to evaluate the structure, morphology, mechanical properties and adhesion of boron nitride thin films deposited on various steel substrates in terms of obtaining stable coatings with good adhesion to the substrate, likely to be used in tribological applications.

Morphology of the surface of coatings and preliminary phase composition without phases identification were analyzed by means of atomic force microscopy (Veeco Multi-Mode AFM Nanoscope IIIa, USA). AFM was working in tapping mode, with simultaneous phase analysis of examined sample (Fig. 3). Precise phase identification was conducted by means of Fourier transform infrared spectroscopy FTIR (Perkin Elmer Spectrum GX, USA – Fig. 4.), which is the most important and widely used tool for characterizing BN films.

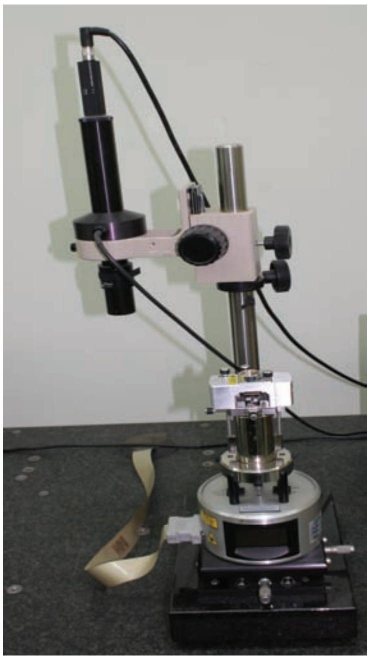

Fig. 3. Veeco Multi-Mode AFM Nanoscope IIIa (IOE MUT)

Fig. 4. FTIR Perkin Elmer Spectrum GX Spectrometer (IOE MUT)

Nanohardness and elastic modulus of the coatings were examined by using NanoAnalyzer – the scanning force microscope (SFM) working in a regime of rigid contact between tested surface and cantilever with high bending stiffness. The testing set, NanoAnalyzer and cantilever are shown in Fig. 5, 6 and 7.

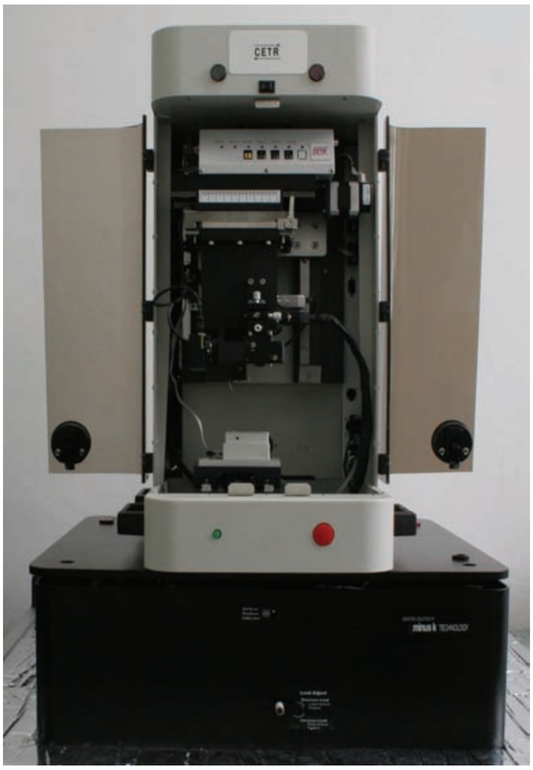

Fig. 5. Universal Nano & Micro Tester (IMVT MUT)

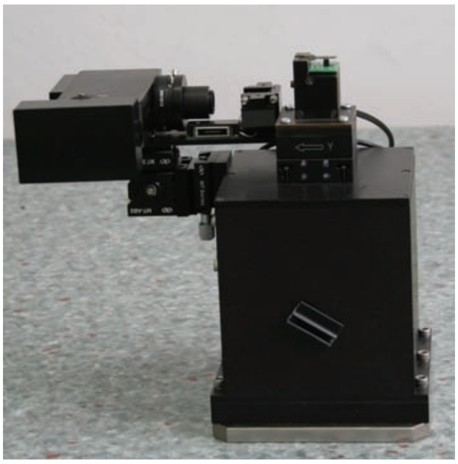

Fig. 6. NanoAnalyzer (IMVT MUT)

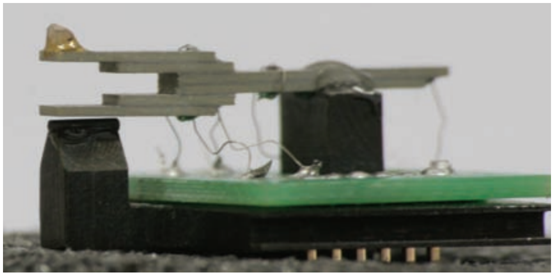

Fig. 7. Cantilever

Coatings nanohardness was carried out by sclerometric method. In this method scratch with constant load is produced and then the average width of the scratch is measured. On the basis of calibration curve (width of scratch versus load) created for material of known nanohardness, the hardness for tested material is calculated. For examined coatings scratches with loads from 700 to 3600 μN were produced. Maximum depth of scratches did not exceed 150 nm (about 20% of coating's thickness) allowing to eliminate or significantly reduce the influence of substrate's properties on obtained results.

Elastic modulus (Young's modulus), unlike nanohardness was measured pointwise in several dozen points by using so-called approach curves. The oscillating probe is moved down to the sample surface. When the tip interacts with the surface, the resonant frequency of oscillation changes due to the forces of elastic repulsion. Frequency change is recorded for every probe position, forming the approach curve. The approach curves for different materials have the different slope. The slope of the curve is proportional to the value of elastic modulus in the area of contact. Described method allows to measure elastic modulus of coatings with a thickness of 1nm practically.

Adhesive measurements of boron nitride thin films to steel substrates were carried out by scratch tests. During the tests, Rockwell indenter with radius of 200 μm scratched the surface of the coatings at the distance of 1.5 mm and constant speed of 3 mm/min with increasing load applied vertically to the indenter. Scratches were produced with simultaneous recording of friction force and acoustic emission. Critical loads for examined BN thin films were determined on the basis of microscopic observations and friction force and acoustic emission runs.

4. Results and discussion

Figure 8 shows morphology of surface and, presented with pseudo-colours, phase map of tested coatings. The surface of the coatings is well-developed and is characterized by fine-grained crystalline structure with grain boundaries clearly marked (Fig. 8). The resulting phase maps indicate that the boron nitride thin films have two-phase, and even three-phase structure (AISI M2 steel).

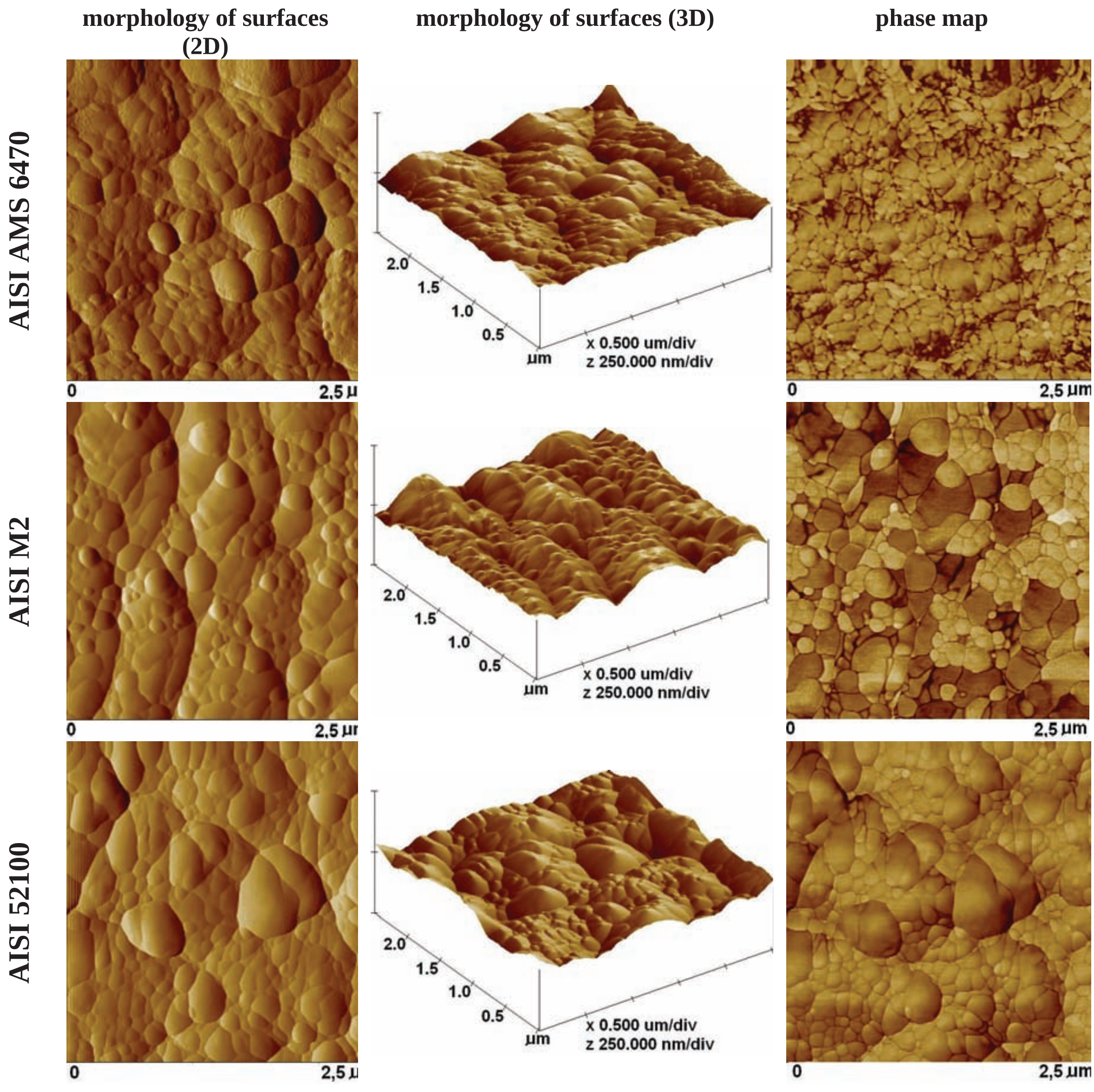

Fig. 8. Morphology of the surfaces and phase composition (AFM)

Fourier transform infrared spectroscopy (Fig. 9) confirmed presence of crystalline phases of boron nitride – soft hexagonal BN (wavenumbers 820 and 1400cm^{-1}) and hard phases (wBN, cBN). In case of hard phases, obtained spectra require deeper analysis. Characteristic wavenumber for cBN phase is 1060cm^{-1}, the occurrence of ~1085, 1125 and 1250cm^{-1} peaks (the first one is the most intensive) indicates presence of wBN. Due to the small difference between the peaks of 1085cm^{-1} (wBN) and 1060cm^{-1} (cBN), the absence of the peaks of 1125 and 1250cm^{-1} in the spectrum of cubic boron nitride can be used to distinguish both hard phases [1]. The fact that the spectra obtain 1260cm^{-1} peak (Fig. 9) suggests the presence of wBN or both hard phases. Considerable intensity of 1050cm^{-1} peak and clearly seen multiphase structure (AFM images) indicate that the highest content of hard phases has the coating deposited on AISI M2 steel substrate. The presence of both soft and hard phases may by advantageous in terms of application of thin BN films as a lubricating coatings.

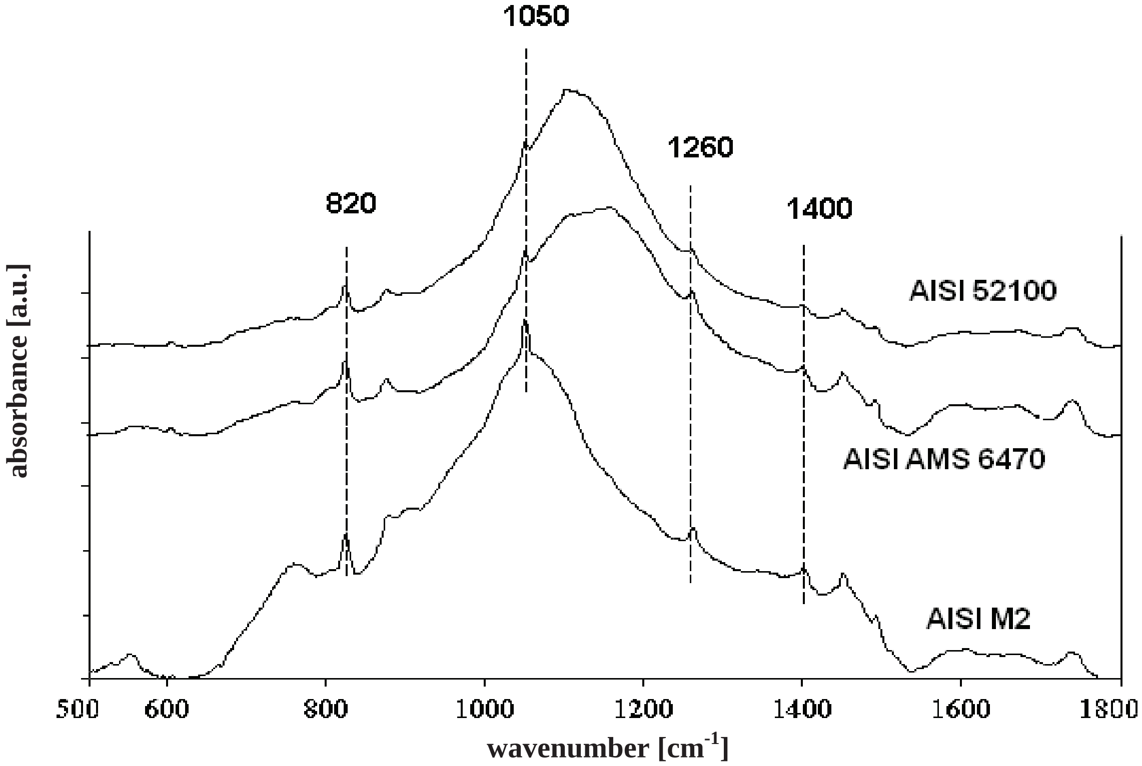

Fig. 9. FTIR spectra of BN coatings

The next stage of the study was to asses the mechanical properties of BN films. The coatings deposited on nitriding steel and bearing steel are characterized by the similar hardness of 5 GPa. Hardness of the coatings deposited on high-speed steel proved to be more than twice higher than for other materials (Fig. 10). It correlates well with a higher content of hard phases in coatings estimated on the basis of results of AFM and FTIR phase analysis.

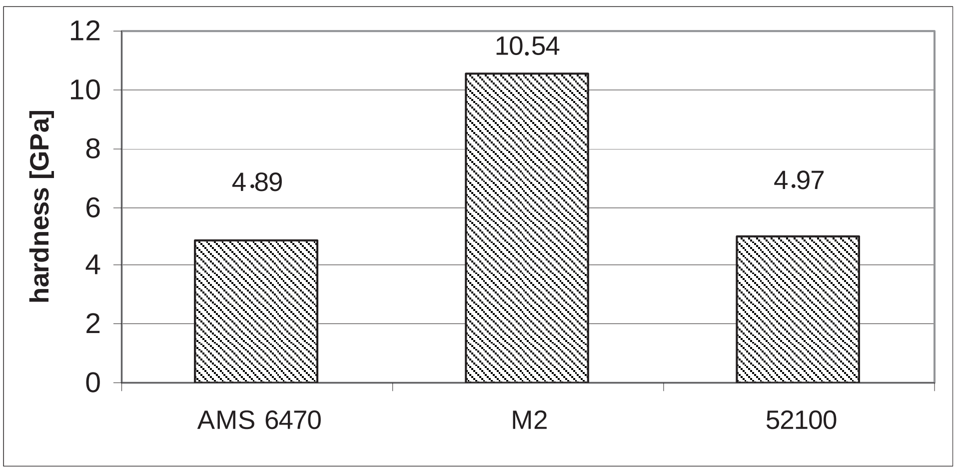

Fig. 10. Nanohardness of BN coatings

Results of Young’s modulus measurements obtained by approach curves method confirmed two-phase structure of deposited BN films. For each examined sample Young’s modulus was characterized by two values of approximately 65 and 92 GPa. (Fig. 11).

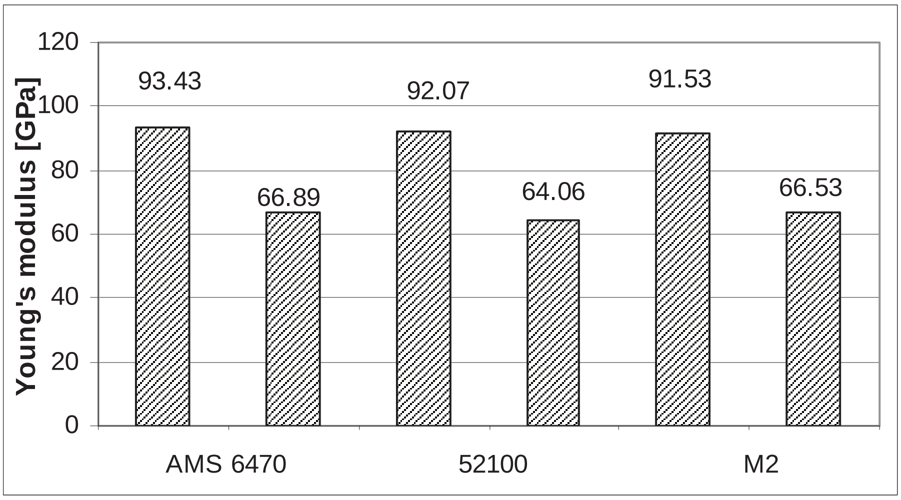

Fig. 11. Young's modulus of BN coatings

In order to investigate the adhesion of BN coatings, the series of scratch tests were carried out. On the basis of microscopic analysis of scratches, friction force and acoustic emission the critical loads for each sample were determined. The example result of scratch test for coating deposited on AISI 52100 steel substrate in shown in Figure 12.

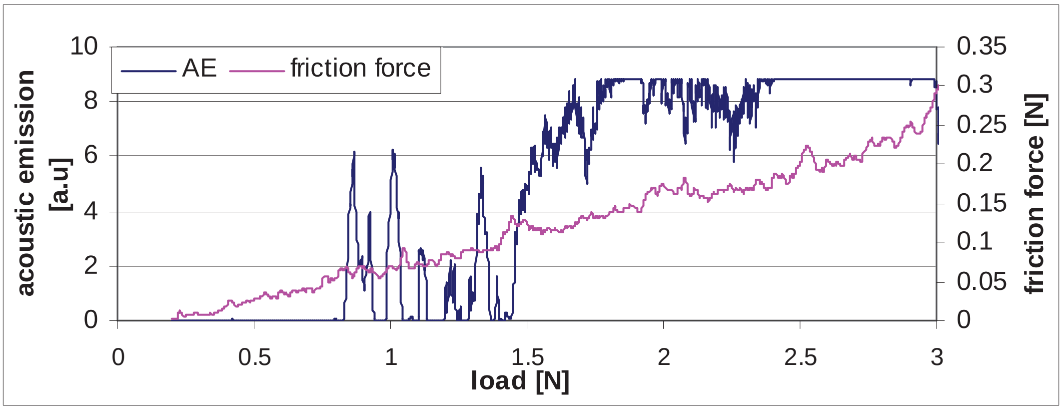

Fig. 12. Friction force and acoustic emission as a function of load for coating deposited on AISI 52100 steel

The coatings deposited on AMS 6470 and M2 substrates characterize by much better adhesion than deposited on 52100 steel, as evidenced by twice higher value of critical load L_c (Fig. 13).

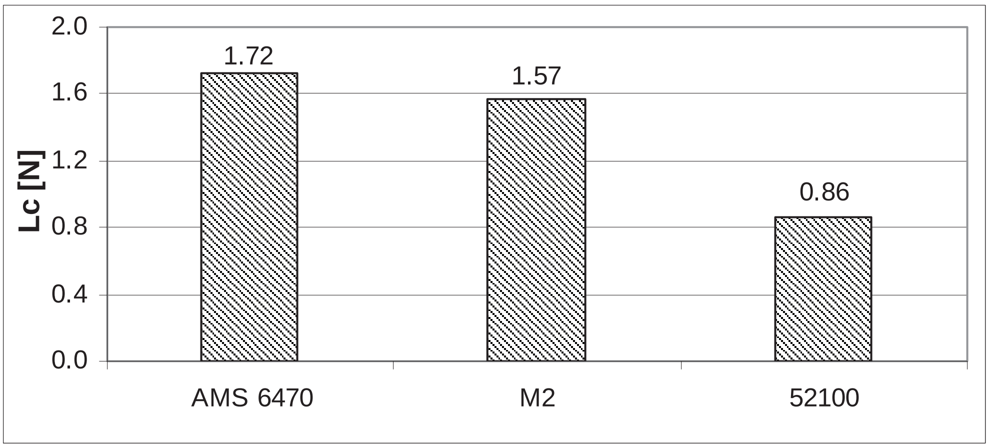

Fig. 13. Critical loads for BN coatings

5. Summary

On the basis of carried out tests and analysis of obtained results the following conclusions can be formulated:

- obtained thin boron nitride coatings have well-developed surface with fine-grained crystalline structure;
- phase analysis (AFM and FTIR) and investigation on mechanical properties (hardness, Young's modulus) proved that obtained coatings has two-phase structure, with presence of soft hBN phases and hard wBN (or wBN+cBN) phases, what may be advantageous in tribological applications of these coatings;
- examined coatings posses different adhesion to the substrates, in case of 52100 bearing steel critical load was twice smaller than other materials.

In the next stage tribological properties of BN coatings will be examined, in particular in terms of wear resistance and friction coefficient between coatings and steel.

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