NANOMECHANICAL TESTING OF AN a-C:N NANOLAYER PREPARED BY ION BEAM ASSISTED DEPOSITION ON Ti6Al4V ALLOY

VLCAK Petr[1], SEPITKA Josef[1], HORAZDOVSKY Tomas[1], JIRKA Ivan[2], GREGORA Ivan[3], NEMEC Michal[1]

[1]Faculty of Mechanical Engineering, Czech Technical University in Prague, Czech Republic, EU
[2]J. Heyrovský Institute of Physical Chemistry, Acad. Sci. CR, v.v.i., Czech Republic, EU
[3]Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic, EU

Abstract

It is well known that carbon-based materials have large variance in hardness. There are several methods for modifying the properties and improving the hardness of carbon-based layers. We applied ion beam assisted deposition for preparing a-C:N nanolayers on Ti6Al4V alloy. A Hysitron TI 950 TriboIndenter™ nanomechanical test instrument was used to assess the depth profiles of the mechanical properties on modified titanium substrates. Two methods were employed in the measurements: a) quasistatic partial unload, and b) dynamic Continuous Measurement of X (CMX). We obtained comparable results from both methods. The average nanoindentation hardness increased from HIT ~ 5GPa for a reference sample to HIT ~ 8.6 GPa for a sample coated by an a-C nanolayer, and to HIT ~ 11.5 GPa for a sample coated by an a-C:N nanolayer. The average storage modulus of the sample coated by a-C:N increased from E´~130 GPa (reference sample) to E´~155 GPa. The storage modulus of the sample coated by the a-C nanolayer was less than the storage modulus of the titanium substrate.

Keywords: Nanolayer, Nanohardness, Nanoindentation

1. INTRODUCTION

This paper deals with an investigation of the mechanical properties of Ti6Al4V alloy coated by amorphous carbon nanolayers, with nitrogen incorporation (a-C:N) and without nitrogen incorporation (a-C). This titanium alloy has many advantages (e.g. high tensile strength, biocompatibility, low elastic modulus), but it has poor tribological properties [1, 2]. Carbon-based layers are often used for improving the friction behavior of titanium alloys [3]. The well-known large variance in hardness of low friction carbon-based materials can be modified by ion bombardment during the deposition process. There are several deposition methods, for example, plasma enhanced chemical vapor deposition (PECVD), filtered cathode vacuum arc deposition (FCVA), and ion beam assisted deposition (IBAD) [4, 5]. The properties of carbon-based materials depend on the type of bonding between the atoms and on the chemical composition, which is influenced by the deposition conditions. We applied nitrogen ion beam assisted deposition to prepare a-C:N nanolayers on Ti6Al4V alloy. The chemical composition and the C-C bonds of a-C:N nanolayers were investigated by glow discharge optical emission spectroscopy (GDOS) and by Raman spectroscopy. The mechanical properties of the modified Ti6Al4V samples were investigated by nanoindentation testing. In our work, we present hardness improvement to the reference titanium alloy. The results of two methods for measuring the mechanical characteristics are evaluated.

2. EXPERIMENTAL PART

The substrates polished on one side were made of Ti6Al4V titanium alloy in the form of a cylinder 20 mm in diameter and 8 mm in height. The substrate roughness after polishing was Ra = 0.02 μm. The substrates were cleaned in organic solvents by means of ultrasound. The deposition of a-C:N nanolayers proceeded by electron beam evaporation of a carbon tablet with simultaneous nitrogen ion bombardment. The deposition of a-C nanolayers proceeded by electron beam evaporation of a carbon tablet without ion bombardment. The

thickness of the nanolayer was measured by a thickness monitor located in the vacuum chamber, and was approximately 100 nm. The a-C:N nanolayers were irradiated with nitrogen ions with energy of 700 eV for structure modification. Both electron beam evaporation and nitrogen ion bombardment were carried out in the apparatus which is presented schematically in **Fig. 1**.

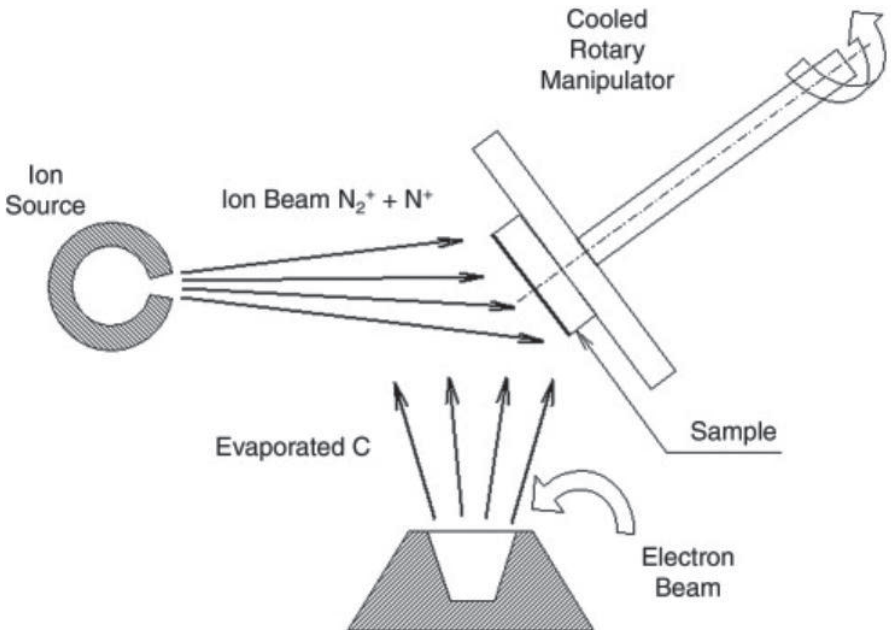

Fig. 1 Schematic representation of the apparatus for ion beam assisted deposition

The chemical composition was measured by means of glow discharge optical emission spectroscopy (GDOS). The Raman spectra were measured using a Renishaw RM 1000 Raman microscope with Ar laser excitation at 514.5 nm.

The TI 950 TriboIndenter® nanomechanical instrument [Hysitron Inc., Minneapolis, USA] in the dual head setup was used for depth profiling of the modified samples. The partial unload function and Continuous Measurement of X (CMX) were applied to the samples. The partial unload approach requires elastic-plastic

$$A = C_0 h^2 + C_1 h^1 + C_2 h^{1/2} + C_3 h^{1/4} + C_4 h^{1/8} + C_5 h^{1/16} \quad , \qquad (1)$$

deformation during gradual force cycles in order to analyze each unloading segment according to the Oliver & Pharr method (**Fig. 2**). Automated analysis plots the depth profile as discrete datasets. Being a dynamic approach, CMX enables continuous dynamic measurements during quasistatic penetration (**Fig. 3.**). Thus, a continuous depth profile can obtained based on nanoDMA analysis. The data were processed by standard polynomial tip area function characteristics for the standard Berkovich shape of a 3-sided pyramid:

where C_0 = 24.5, C_1 = 5350.82, C_2 = -1.5891E+5, C_3 = 1.3072E+6, C_4 = -2.9643E+6, C_5 = 1.8198E+6. The values of the constants $C_{0\text{-}5}$ were obtained from nanoindentation of the fused silica [6]. The partial unload load function was composed of 33 loading and unloading segments with increasing peak force, followed by 50% of unload. Each unloading segment is analyzed for elastic modulus and hardness, and can be plotted versus the depth, resulting in a depth profile of the mechanical properties. The begin and peak force were set to *Pmin* = 15 μN and *Pmax* = 3000 μN, respectively. A small dynamic force oscillation is continuously superimposed on a quasistatic force during loading. The harmonic force and displacement signal is analyzed according to standard nanometric dynamic mechanical analysis, which gives a variety of mechanical parameters such as hardness, storage modulus, loss modulus, etc. (**Fig. 3**). The begin and peak force were set to *Pmin* = 15 μN and *Pmax* = 3000 μN, respectively. The begin and peak dynamic force were set to Pmin = 12 μN and *Pmax* = 170 μN, respectively. The frequency was *f* = 85 Hz. A matrix of 4x4 indents with separation of 5 μm between each indent was applied to each sample for each nanoindentation setup.

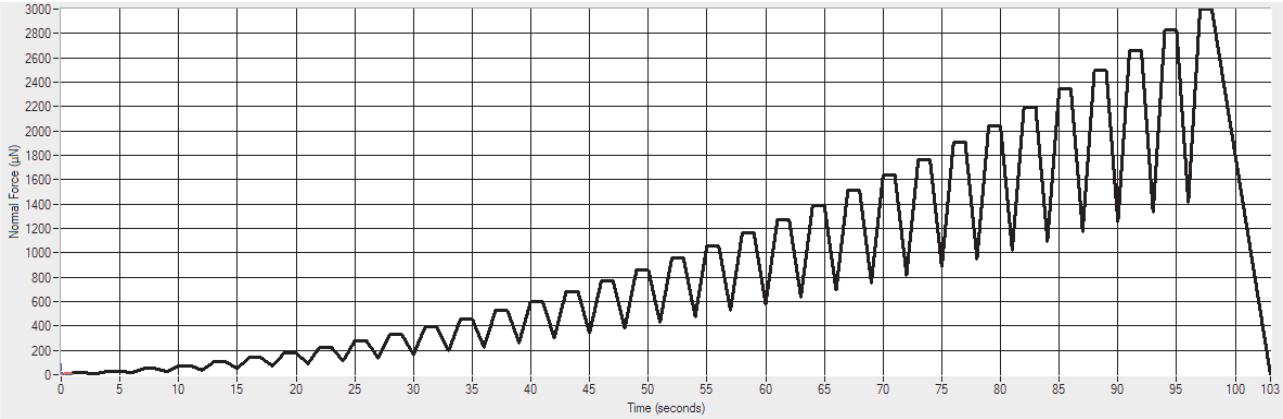

Fig. 2 Partial unload load function

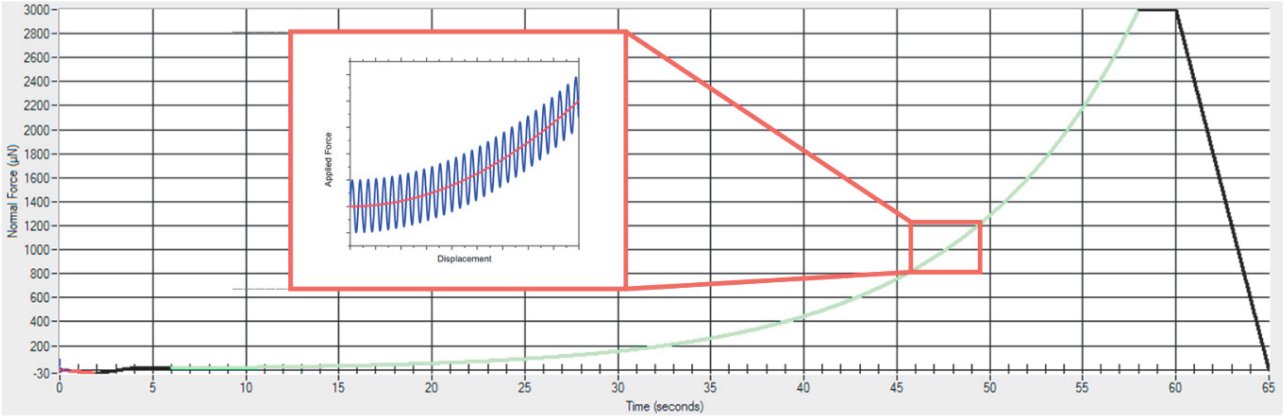

Fig. 3 Continuous Measurement of X

3. RESULTS AND DISCUSSION

A quantitative analysis of the GDOS measurements showed the elemental concentrations of carbon and nitrogen in the a-C:N nanolayer. The carbon concentration ranges from 50 to 70 at%, and the nitrogen concentration ranges from 30 to 50 at%.

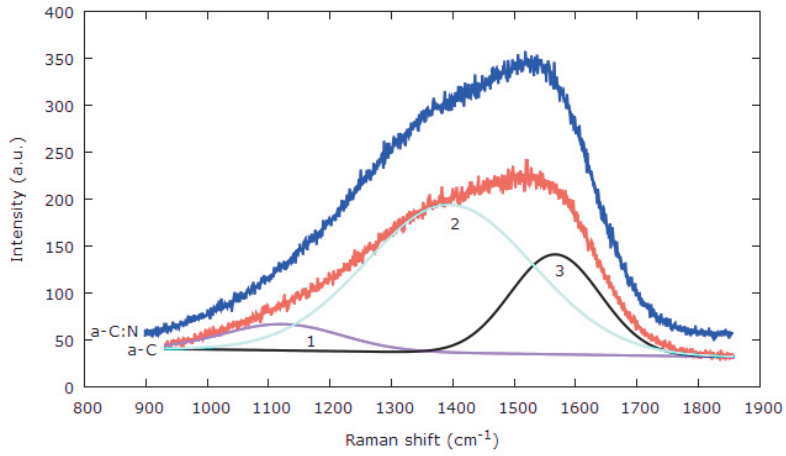

Fig. 4 Raman spectra of amorphous carbon nanolayer bombardment with nitrogen ions (a-C:N) and without ion bombardment (a-C)

The Raman spectra in **Fig. 4** have one main peak located at ~1500 cm−1. The spectra were decomposed by fitting to three Gaussian curves. The Raman spectra in **Fig. 4** have a DLC (diamond-like carbon) character; that is, they are composed of the D peak (disordered graphitic carbon **-** peak 2 at ~1400 cm-1) and the G peak (graphitic carbon - peak 3 at ~1565 cm-1). A small significant peak 1 at ~1100 cm-1 has been associated with nanocrystalline diamond. The results indicate that the a-C:N and a-C nanolayer have a predominantly graphitic character. The ratio of the integrated areas under the peak 1, 2 and 3 is 2.7 for the a-C:N nanolayer and 3.1 for the a-C nanolayer. The correlation with the nanoindentation hardness results shows that the nanoindentation hardness increases as the ratio of the integrated areas decreases, which is in agreement with the literature [7].

We obtained the depth profiles of the mechanical properties represented by storage modulus $E´$ and nanoindentation hardness H_{IT} (**Fig. 5** and **6**). The reference sample has a gradient of the mechanical properties to the contact depth of h_c ~ 6 nm. A similar trend was observed for the a-C:N sample at shallow indentation depths (**Fig. 5**). This could result from the mechanical preparation of the surface or tip area function calibration. The results in **Fig. 5** and 6 show that the two nanomechanical testing methods (quasistatic partial unload and dynamic Continuous Measurement of X) provide comparable trends and values of the mechanical characteristics. The minimum indentation depth at which we are able to obtain the mechanical properties of both methods are limited by the sharpness of the tip and by the roughness of the sample surface. The values of $E´$ and H_{IT} are calibrated from h_c ~ 8 nm and from h_c ~ 25 nm, respectively.

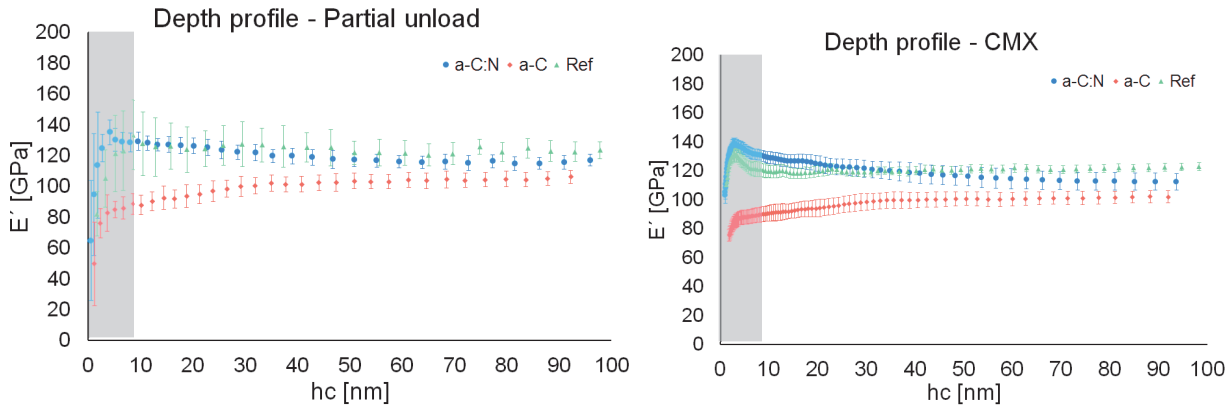

Fig. 5 Depth profiles of the storage modulus. Left **-** Partial unload results. Right **-** Continuous Measurement of X. Values of $E´$ are calibrated from depths of h_c = 8 nm. The grey rectangle demarcates uncalibrated data

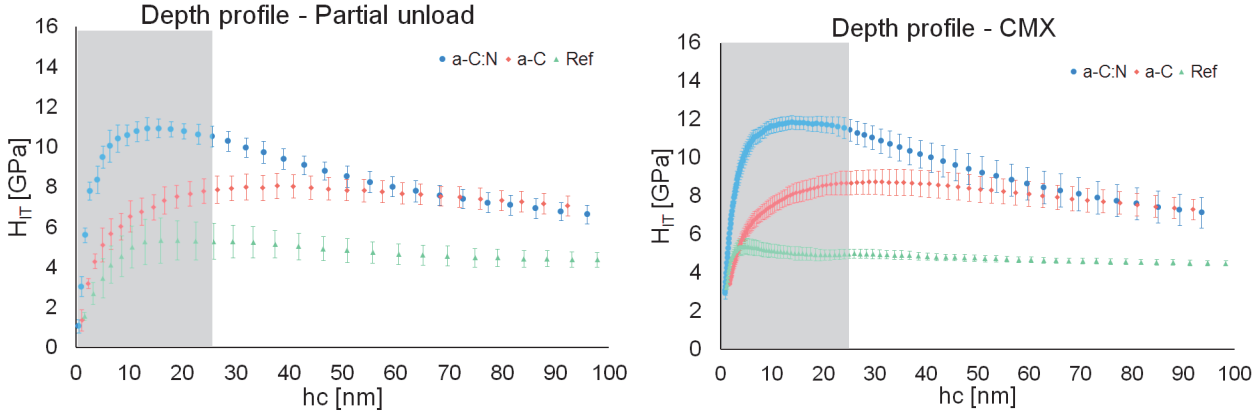

Fig. 6 Indentation hardness, the values of H_{IT} are calibrated from depths of h_c = 25 nm. The grey rectangle demarcates uncalibrated data

The maximum values of the storage modulus E' = 130.7 GPa and of the nanoindentation hardness H_{IT} = 11.5 GPa were measured on the a-C:N sample at contact depths of h_c ~ 8 nm and h_c ~ 26 nm, respectively. The a-C sample had maximum storage modulus values of E' = 100 GPa and nanoindentation hardness values of H_{IT} = 8.6 GPa at a contact depth of h_c ~ 92 nm and h_c ~ 37 nm, respectively. Both measured layers have greater indentation hardness than the reference sample in the whole depth profile. The maximum indentation hardness of the reference sample is H_{IT} ~ 5 GPa. The a-C:N sample has higher values of H_{IT} than the a-C sample to a contact depth of h_c ~ 77 nm. H_{IT} of the a-C:N has a sharply decreasing trend with increasing h_c, whereas the depth profile of H_{IT} of the a-C sample has a constant trend. The results show that the CMX method gives a large number of points and lower variance values than quasistatic partial unload. The large number of points provides reliable information on the trend change of the measured characteristics. This may be advantageous for measurements of a nanolayers, multilayered structures and structures with a variable gradient of mechanical characteristics.

4. CONCLUSION

Two methods were employed in measurements of the mechanical characteristic of a-C:N and a-C nanolayers on a Ti6Al4V substrate: a) quasistatic partial unload, and b) dynamic Continuous Measurement of X (CMX). The results showed that the two methods give comparable trends and values of the measured characteristics. The CMX method provides a large number of points and lower variance values than quasistatic partial unload. This may be advantageous for measurements of multilayered structures and structures with a variable gradient of mechanical characteristics. We obtained an increase in nanoindentation hardness from H_{IT} ~ 5 GPa for the reference sample to H_{IT} ~ 8.6 GPa for a sample coated by a-C nanolayer, and to H_{IT} ~ 11.5 GPa for a sample coated by a-C:N nanolayer. The average storage modulus of the sample coated by a-C:N increased from E'~130 GPa (reference sample) to E'~155 GPa.

ACKNOWLEDGEMENTS

This research has been supported by Ministry of Education, Youth and Sports of the Czech Republic Project SGS15/186/OHK2/3T/12 of the CTU in Prague.

REFERENCES

[1] GEETHA M., SINGH A. K., ASOKAMANI R., and GOGIA A. K. Ti based biomaterials, the ultimate choice for orthopaedic implants-a review, Progress in Materials Science, Vol. 54, No. 3, 2009, pp. 397-425.

[2] PODZIMEK S., TOMKA M., NEMETH T., HIMMLOVA L., MATUCHA P., PROCHAZKOVA J. Influence of metals on cytokines production in connection with successful implantation therapy in dentistry, Neuroendocrinology Letters, Vol. 31, No. 5, 2010, pp. 657-662.

[3] VLCAK P., CERNY F., WEISS Z., DANIS S., SEPITKA J.,TOLDE Z., JECH V. The effect of nitrogen ion implantation on the surface properties of Ti6Al4V alloy coated by a carbon nanolayer, Journal of Nanomaterials. Vol. 2013, No. NNTA, Art. No. 475758, 2013, pp. 1-8, Doi:10.1155/2013/475758.

[4] TRAVA-AIROLDI V. J., BONETTI L. F., CAPOTE G., SANTOS L.V. and CORAT E. J. A comparison of DLC film properties obtained by r.f. PACVD, IBAD, and enhanced pulsed-DC PACVD, Surface and Coatings Technology, Vol. 202, no. 3, 2007, pp. 549-554.

[5] WANG G., ZHANG H., LI W., YANG F., CUI L., ZUO H., HAN J. The preparation and evaluation of graded multilayer ta-C films deposited by FCVA method, Applied Surface Science, Vol. 257, 2011, pp. 5064-5069.

[6] OLIVER W. C. and PHARR G. M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, Journal of Materials Research, Vol. 7, No. 6, 1992, pp. 1564-1580.

[7] ZIEBERT C., RINKE M., STÜBER M., ULRICH S., HOLLECK H. Interfaces and temperature stability of stepwise graded DLC films studied by nanoindentation and Raman spectroscopy, Surface and Coatings Technology, Vol. 200, 2005, pp. 1127-1131.