ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 20, No. 1. 2014

Multicomponent Thin Films Deposited by PVD ARC and LARC Technology

Dagmar JAKUBÉCZYOVÁ *, **Marek KOČÍK, Pavol HVIZDOŠ**

Institute of Materials Research of the Slovak Academy of Sciences, Watsonova 47, 04001 Košice, Slovakia

http://dx.doi.org/10.5755/j01.ms.20.1.3716

Received 08 March 2013; accepted 08 July 2013

The paper is focused on a comparison of advanced layers deposited by two coating technologies – cathodic arc deposition (ARC) and lateral rotating cathodes (LARC). For characterization standard analyses were selected: the determination of the layer wear resistance by Calotest method, specification of the depth concentration profiles of constituting elements from the coating surface down to the substrate, and measurement of the nanohardness at dynamic loading. The thickness of the CrTiN layer reached 1380 nm – 1740 nm and that of the multi/nanolayers AlXN3 was 2630 nm – 3160 nm. The coating nanohardness on the surface attained 39 GPa for AlXN3 (X = Cr), 33 GPa for CrTiN and 12.5 GPa for the substrate. Only at coating prepared by LARC-Technology it is possible to create the multilayers of nanometric dimensions. AlXN3 coating was formed by 48 layers with dimensions of 58 nm – 70 nm. These nanolayers lead to the increase of system toughness as they prevent the crack propagation. Their application on the tools and components promises to increase their durability under service conditions.

Keywords: thin films, PVD, calotest, GDOES, nanohardness.

1. INTRODUCTION

Concepts and coating technologies of materials and components have had a rapid development during the last years. If the first PVD TiN coatings were prepared early in 1980 and in 1988 were added only next 2 types (TiCN a CrN), in the year 2000 it was possible to find approximately 14 basic types of PVD coatings. At the present time there exist more than 70 types of coatings on the market, when we consider as difference criterion only their chemical composition [1, 2]. The differences are mainly in the coating structure, specifically in their micro up to nanosized dimensions. Variability in the structure is achieved in multi- and nanolayered systems, eventually in so called gradient structure. Finally, the important parameters are the final coating properties and its working properties that depend of course also on their microstructure. It has been established that with multilayered structure it is possible to achieve higher durability of the tool at interrupted cutting (individual layers act as an effective barrier against microcracks propagation), while on the other hand at stable cutting monolayer that has usually higher temperature stability and lower coefficient of friction is more suitable [3]. The reactive substrate surface must be perfectly prepared with recommended roughness in order to attain the superior deposition of the coating on the material. For application of layers at present it is valid that the first layer has to fulfil the condition of optimal adhesion, which it is possible to provide by Ti + TiN or Cr-CrN coatings [1].

Chromium nitride (CrN) has become recently very popular as a coating material for tools and similar products [4, 5]. Chromium nitride coatings have been successfully made using various types of physical vapour deposition (PVD) processes, such as cathodic arc deposition (ARC technology) [6, 7]. On top of this coating there can be further deposited layers based on Al-Ti-N, but only up to particular physical limits of Al content. At about 70 % Al the cubic lattice changes to the hexagonal one, which is not very suitable for machinability because of low wear resistance. It is possible to overcome these physical limits by addition of thermal and oxidation resistant elements such as Cr, Si, etc. [3].

The last layer has to resist the thermal-oxidation effects and has to have sufficient hardness and also wear resistance. For preparation of more complex coating types, such as gradient and multilayered ones, modern techniques of low voltage arc deposition with rotating (non alloyed) cathodes have been developed. These advanced coatings utilize advantages of conventional layers (TiN, CrN, TiAlN, AlTiN) as well as nanocomposite coatings (nc-TiAlN/a-SiN, nc-AlCrN/a-SiN, etc.) [1]. It is possible to prepare them by LARC (lateral rotating cathodes) and CERC (central rotating cathode) methods. Here, the electrodes are located at the door of the chamber (LARC) or at its middle part, centrally with respect to the coated parts (CERC).

Another option is a combination of the central and the lateral positioning of the electrodes, where it is possible to change their number, and sometimes also their type [2, 8, 9].

2. EXPERIMENTAL

Coating deposition was realised on the material PM HSS S390, (Böhler) in form of discs with dimensions of Ø 30 mm × 6 mm. The substrate was prepared by the standard metallographic technique (grinding and polishing) to the roughness R_a ~4 nm. CrTiN and AlXN3 coatings were applied by two PVD technologies: by reactive arc evaporation – ARC method (cathodic arc deposition) and LARC technology (lateral rotating cathodes). CrTiN coating was deposited by the ARC method as a monoblock with an adhesive TiN layer [10] and AlXN3 (X = Cr) coating by LARC method as multilayer [11]. The thickness

---

[*] Corresponding author. Tel: +421-55-7922414, fax: +421-55-7922408.
E-mail adress: *jakubeczyova@gmail.com* (D. Jakubéczyová)

of coatings was determined by Calotest, which is a suitable additional method how to obtain quick information about layer configuration and abrasion resistance.

Rotating steel ball with diameter of approx. 25 mm forms a trace on the specimen surface. The trace called calotte is observed and measured by light microscope and allows to calculate the layer thickness and also to monitor relevant changes and failure of the layer at transitions between layers up to the substrate. The method is described in detail in [12, 13]. For qualitative and quantitative determination of metallic and non-metallic elements through a cross section of applied layers GDOES method (glow discharge optical emission spectroscopy, GDS-750) was used. Its outputs are tabular values and vertical concentration profile allowing a graphical record of the concentration changes of selected elements up to the depth of 0.1 mm of the investigated material. Selection of individual wavelengths for analytical purposes is subject to some steps, which are listed in the methods described in [14 – 17].

Nano hardness of coatings CrTiN and AlXN3 deposited on the substrate S390 was measured by depth sensing indentation. The tests were carried out employing a nano hardness tester TTX-NHT (CSM Instruments, Switzerland). We used a Berkovich indenter (three-sided pyramid) operated in a dynamic sinusoidal mode with maximum load of 400 mN and loading rate 800 $mN \cdot min^{-1}$.

The results obtained were processed by the method of Oliver and Pharr [18]. This method is suitable for the characterization of coatings and thin layers as it allows, under certain conditions, to separate the values corresponding to layers and the substrate. Each specimen was subjected to minimally 20 indentations and the results were processed statistically.

3. RESULTS AND DISCUSSION

Both coatings were subjected to fractographic analysis employing an SEM technique with EDS that was performed on the fracture surface after bending test. The surface of fractures was examined macroscopically and microscopically.

Figs. 1, a, and 1, b, represent the cross-section of the CrTiN–S390 and AlXN3–S390 systems. In both cases there are visible adhesive layers above the substrate: TiN is a base for CrTiN and CrN is a base for AlXN3, which was confirmed by line EDS analysis, as shown in Figs. 2, a, and 2, b.

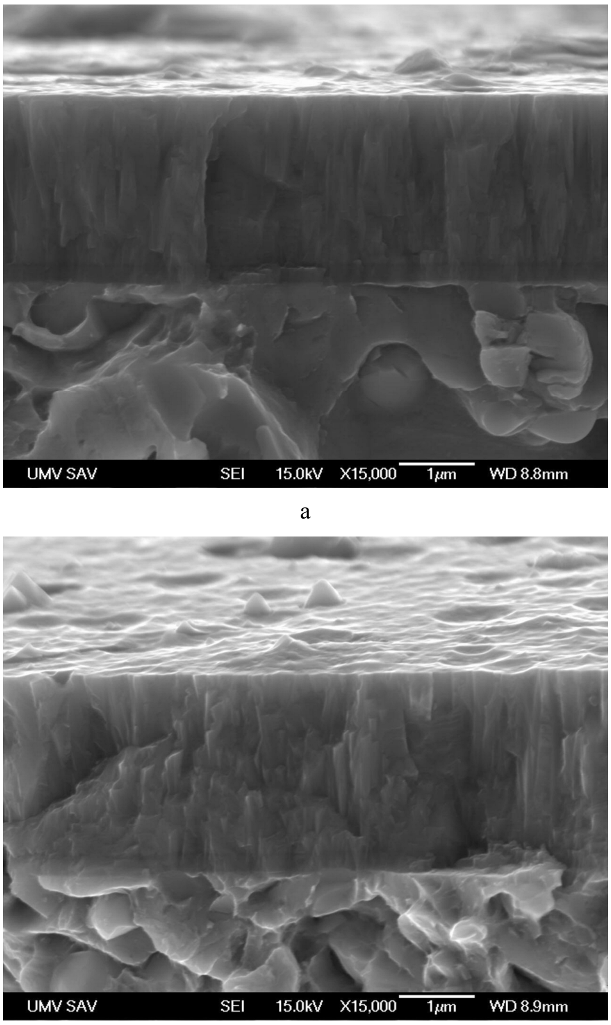
Figs. 3a, b, c, represent the trace after the Calotest, the so called calotte, and a principle of thickness determination for CrTiN layer based on measurement of D_1 and D_2 diameters and calculation according to the simple equation:[13]:

$$H = D_1 \times D_2 / Ø \text{ ball}. \qquad (1)$$

The thickness of layers deposited as a monoblock reached the values of $h = 1380$ nm – 1740 nm. The calotte in the AlXN3 layer and thickness calculation is illustrated in Figs. 4, a, b, c. In this case the calculated thickness of the layer was $h = 2630$ nm – 3160 nm.

In Fig. 4, b, it is possible to see the layout of AlCrN multi/nanolayers, their number is 48 with the thickness of individual layers of 58 nm – 70 nm. The base AlXN3 layer is CrN, with the best adhesion. The core layer is a nanolayer Al/CrN with a very high degree of toughness and crack absorption and the top layer is a monoblock (AlCrN) with a very high degree of hardness and wear resistance [19].

Depth concentration profiles of the elements, which characterise the investigated layers from the coating surface down to the substrate, were determined by the GDOES method. Fig. 5, a, illustrates a dominant concentration of Cr and concentration profile of Ti and N elements as an adhesive layer above the substrate.



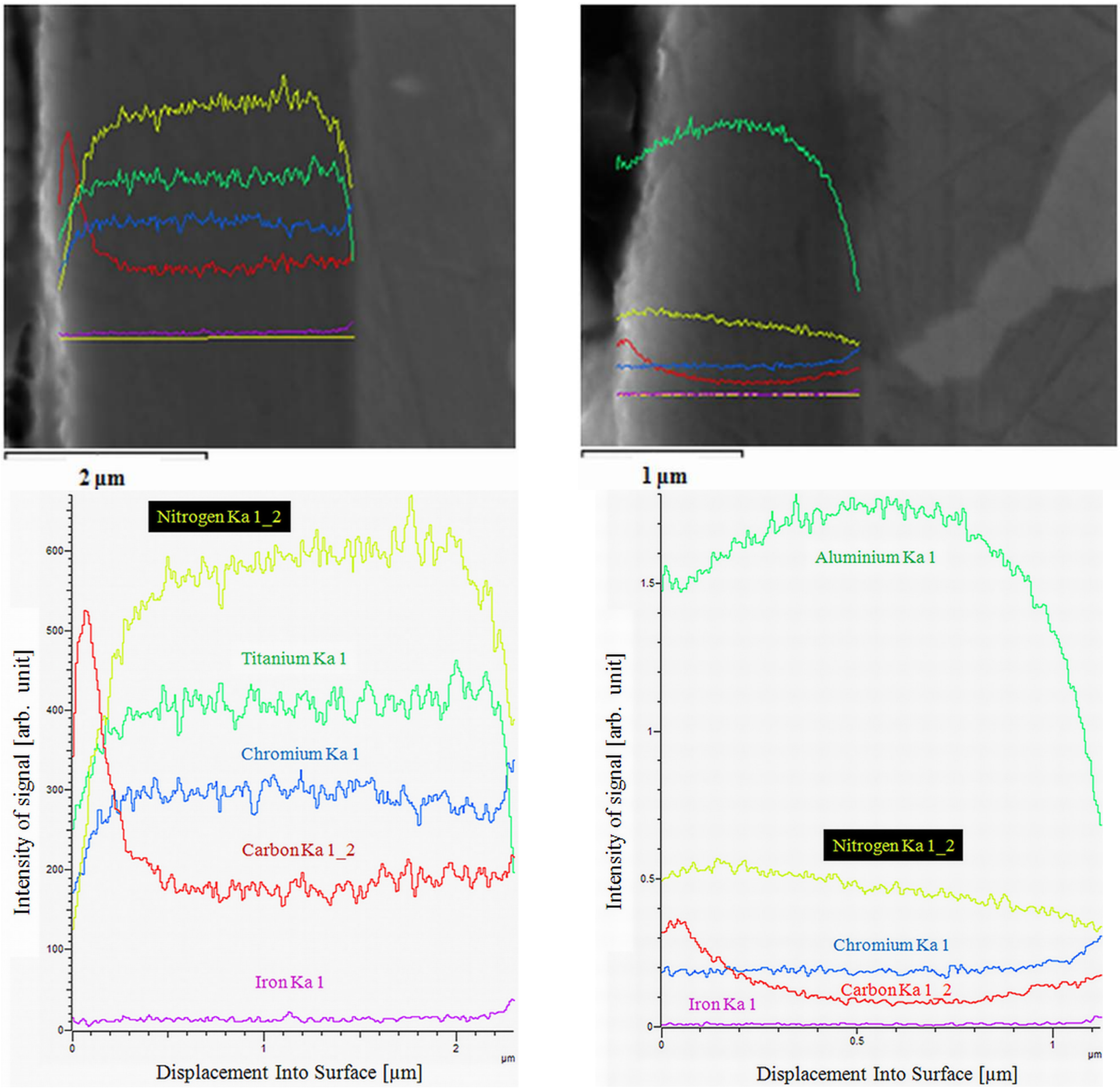
b

Fig. 1. Cross-section (SEM): a – CrTiN–S390 system; b – AlXN3–S390 system

Fig. 5, b, represents "rippling" course of elements in the nanolayers. This analysis complements the information about the coating thickness.

The dependence of the hardness on indentation depth for investigating systems is shown in Fig. 6, a.

The graph illustrates the behaviour of deposited layers in comparison with the substrate. The initial values in the graph relate with the indenter contact with the surface and consolidation of zero position of indenter. The values were measured in accordance with the requirements of the international standard for determination of coating hardness [20]. After indenter consolidation the data



a

b

Fig. 2. Cross–section with line EDS analysis: a. CrTiN–S390 system; b. AlXN3–S390 system

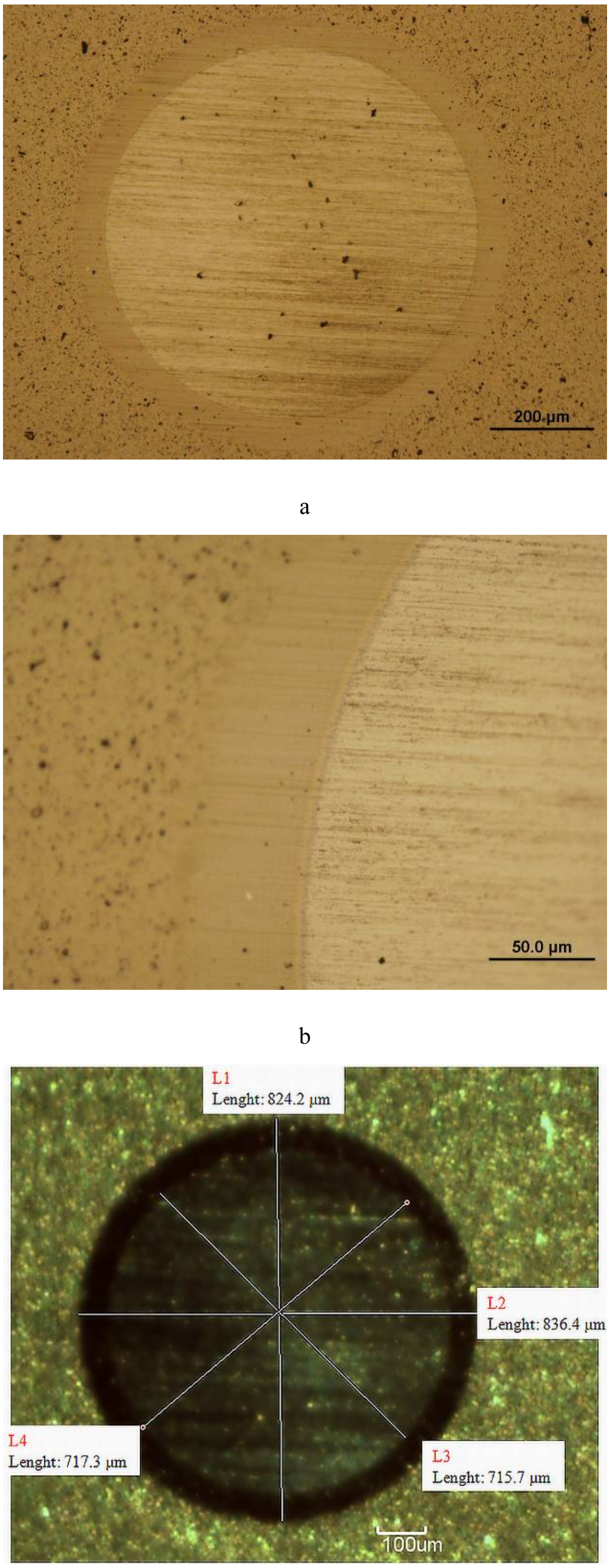
measured at low depths correspond to the hardness values of the investigated coatings. With the increasing load/depth the influence of the substrate started to manifest and the hardness values uniformly decreased for both types of layers. The hardness in the CrTiN layer was about 33 GPa (depth < 200 nm) which decreased down to 17 GPa for depth > 1350 nm. In the AlXN3 layer hardness decreased from 39 GPa (< 200 nm) to 25 GPa in depths > 1200 nm.

The data of the substrate hardness are uniform, without oscillations and with low scatter, which indicates that the specimen surface was well prepared before the deposition and the hardness is approx. 12.5 GPa. Higher hardness values of the AlXN3 layer in comparison with the CrTiN layer hardness are connected with the deposition method.

Beside hardness, from the unloading part of indentation curves it is possible to calculate also indentation elasticity modulus “*E*”, because in this part only elastic response (elastic recovery) takes place. In this way it is possible to map elasticity of individual components of the material system at micrometric level.

Dependence of elastic modulus “*E*” of the experimental materials on depth of indenter imprint at dynamic loading is expressed by the curves in Fig. 6, b.

With decreasing hardness the elastic modulus decreased. It is interesting that at the depth of about 300 nm the elasticity of coatings reached the values equal to that of the substrate and then continued to decrease further which suggests that the substrate had higher ability for elastic recovery. There are many works investigating deformation mechanisms of thin layers by means of nanoindentation, where during loading many various factors influence both coating and substrate. Previous studies showed that hardness and Young’s modulus depend on quantities such as yield strength, adhesion, layer thickness, internal structure and density of the layer and of course geometry of the indenter tip [21 – 23].

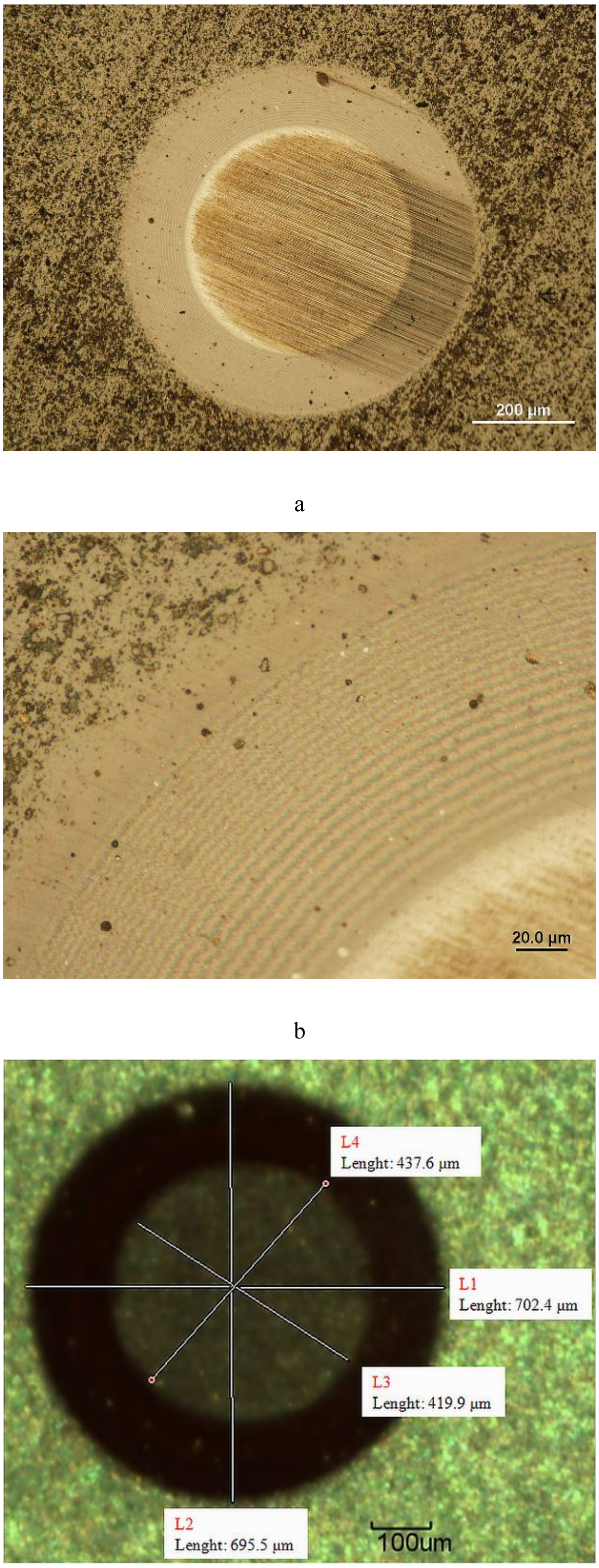


a

b

c

Fig. 3. Calotest in CrTiN layer: a – trace after the test; b – detail; c – measurement of the layer thickness – *h* = (1380 – 1740) nm



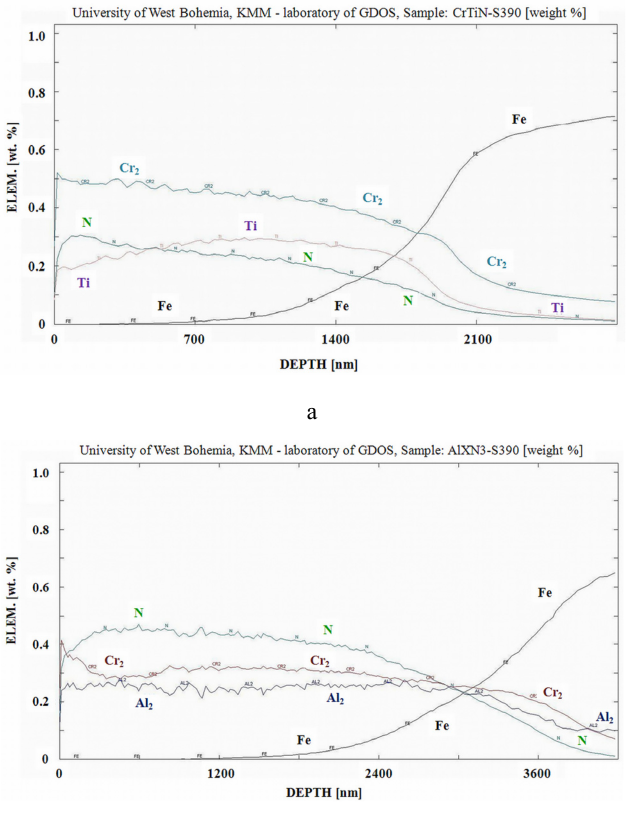
a

b

c

Fig. 4. Calotest in AlXN3 layer: a – trace after the test; b – detail; c – measurement of the layer thickness – *h* = (2630 – 3160) nm

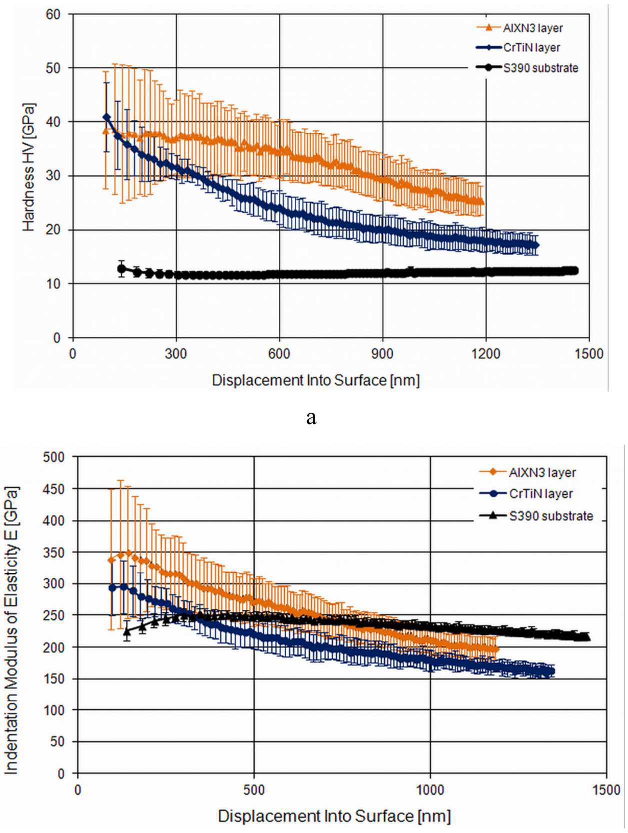
These results allowed us to state that lower values of "*E*" in case of both coatings could be related to chemical composition, internal structure of deposited layers and morphology of grains/crystallites. Lower elastic modulus "*E*" of the multilayer coating most likely resulted from different arrangement of individual layers and concentration of elements across its thickness.



a

b

Fig. 5. Depth concentration profile: a – CrTiN–S390 system; b – AlXN3–S390 system



a

b

Fig. 6. Nanoindentation load-displacement curves relative to: a – hardness; b – Young´s modulus "*E*"

The deposited types of coatings ensured increased hardness and elastic modulus of the base material. The substrate-layer interfaces were without failures, which confirmed excellent adhesion properties of the system. Due to their specific properties, the coatings appear suitable for use in practical operations, as specified in work [24].

4. CONCLUSIONS

The main idea of the contribution is comparison of the of the advanced layers deposited by two coating technologies – ARC and LARC. From the realised analyses the following results can be drawn:

- The thickness of the CrTiN layer deposited by ARC method and analysed by Calotest reached the values.
- *h* = 1380 nm – 1740 nm. The multi/nanolayers AlXN3 coating applied by advanced LARC-technology reached the thickness *h* = 2630 nm – 3160 nm.
- Thanks to the special arrangement of the rotating electrodes in LARC-technology it is possible to create the multilayers of nanometric dimensions. AlXN3 coating was formed by ~48 layers with dimensions of 58 nm – 70 nm. These nanolayers lead to the increase of system toughness as they prevent the crack propagation.
- The depth concentration profile of layers was determined by GDOES method. The base AlCrN3 layer is CrN, with the best adhesion. The core layer is nanolayer Al/CrN with a very high degree of toughness and crack absorption and the top layer is a monoblock (AlCrN) with a very high degree of hardness and wear resistance.
- The coating nanohardness on the surface attained the value of 39 GPa for AlXN3 and 33 GPa for CrTiN. The course of hardness within the layers was uniform with a gradual hardness decrease because of the substrate influence.
- From the beginning, the indentation modulus of elasticity "*E*" showed decreasing tendency with parallel course for both layers. The subsequent course of the value "*E*" is almost the same for all three materials, i. e. at greater depths the influence of elastic response of coatings is negligible.

Both types of coatings were suitable for deposition on the PM high speed steels. Their application on the tools and components promises to increase their durability under service conditions.

Acknowledgments

The authors are grateful for the support of experimental works by the national projects VEGA 2/0060/11 and VEGA 2/0075/13.

REFERENCES

1. http://www.mmspektrum.com/clanek/pocitacova-simulace-rustu-pvd-povlaku-a-nova-rada-trojvrstvych-povlaku.html
2. **Cselle, T., Coddet, O., Galamand, C., Holubar, P., Jilek, M., Jilek, J., Luemkemann, A., Morstein, M.** Triple Coatings$^{3®}$ New Generation of PVD-Coatings for Cutting

Tools *Journal of Machine Manufacturing* XLIX 2009: pp. 19 – 25.

3. **Park, J.-K., Baik, Y.-J.** Thermal Stability of Nano–layered Structure and Hardness of TiAlN/Si_3N_4 Nanoscale Multilayered Coating *Materials Letters* 63 2009: pp. 1674 – 1676. http://dx.doi.org/10.1016/j.matlet.2009.05.006
4. **Djouadi, M.-A., Nouveau, C., Beer, P., Lambertin, M.** CrxNy Hard Coatings Deposited with PVD Method on Tools for Wood Machining *Surface and Coatings Technology* 133 – 134 2000: pp. 478 – 483.
5. **Berg, G., Friedrich, Ch., Broszeit, E., Berger, Ch.** Development of Chromium Nitride Coatings Substituting Titanium Nitride *Surface and Coatings Technology* 86 – 87 1996: pp. 184 – 191.
6. **Lee, J.-W., Duh, J.-G., Wang, J.-H.** Mechanical Property Evaluation of Cathodic Arc Plasma-deposited CrN Thin Films on Fe-Mn-Al-C Alloys *Surface and Coatings Technology* 168 (2 – 3) 2003: pp. 223 – 230.
7. **Wang, D.-Y., Wenig, K.-W.** Deposition of CrN Coatings by Current–modulating Cathodic Arc Evaporation *Surface and Coatings Technology* 137 2001: pp. 31 – 37.
8. http://platit.com/coating-equipment/pl70
9. http://platit.com/coating-equipment/p311?page=0%2C2
10. http://platit.com/coatings/coating-types/optional-coatings/crtin
11. http://platit.com/node/262
12. http://www.csm-instruments.com/en/Calotest
13. http://www.stinstruments.com/uploads/editor/brochures/Calotest.pdf
14. **Settineri, L., Faga, M. G., Gautier, G., Perucca, M.** Evaluation of Wear Resistance of AlSiTiN and AlSiCrN Nanocomposite Coatings for Cutting Tools *CIRP Annals–Manufacturing Technology* 57 2008: pp. 575 – 578.
15. **Vnouček, M.** Povrchové efekty při GDOES. (Surface Effects at GDOES.). PhD Thesis, The University of West Bohemia in Pilsen, 2002 (in Czech).
16. **Jakubéczyová, D., Hagarová, M., Džupon, M.** Experimentálne metódy hodnotenia tenkých vrstiev aplikovaných technológiou ARC a LARC *Transfer Inovácií* 15 2009: pp. 132 – 137 (in Slovak).
17. **Hagarová, M., Bláhová, O., Savková, J.** Structure and Properties of PVD Coatings Deposited by ARC and LARC Technology *Acta Metallurgica Slovaca* 15 2009: pp. 221 – 227.
18. **Oliver, W. C., Pharr, G. M.** Measurement of Hardness and Elastic Modulus by Instrumented Indentation: Advances in Understanding and Refinements to Methodology *Journal of Materials Research* 19 2004: pp. 3 – 20.
19. http://platit.com/multilayer-coating
20. ISO 14577–4. Metallic Materials – Instrumented Indentation Test for Hardness and Materials Parameters – Part 4: Test Method for Metallic and Non-Metallic Coatings, 2007: pp. 1 – 24.
21. **Nakonechna, O., Cselle, T., Morstein, M., Karimi, A.** On the Behaviour of Indentation Fracture in TiAlSiN Hard Thin Films *Thin Solid Films* 447 – 448 2004: pp. 406 – 412.
22. **Logothetidis, S., Kassavetis, S., Charitidis, C., Panayiotatos, Y., Laskarakis, A.** Nanoindentation Studies of Multilayer Amorphous Carbon Films *Carbon* 42 2004: pp. 1133 – 1136.
23. **Picek, R., Boháč, P.** Measurement of Elastic Constants of Thin Films by the Law Method *Materials Structure* 13 2006: pp. 97 – 101.
24. **Misirli, C., Sahin, M., Dinc, M.** Fatigue Properties of AlTiN and TiN-coated High Speed Steels (HSS) Steels *Scientific Research and Essays* 6 (15) 2011: pp. 3200 – 3204.