INFLUENCE OF PLASMA BASED ON IMPLANTATION AND DEPOSITION METHOD ON STRUCTURE, INTERNAL STRESS, MECHANICAL PROPERTIES OF NANO-CRYSTALLINE BIOINERT ZRN COATINGS

Anton Taran[1,a], Igor Garkusha[1,b], Valerij Taran[1,c], Renat Muratov[1], Vadym Starikov[2], Alexey Baturin[2], Svetlana Romaniuk[3] and Athanasios G. Mamalis[4,d]

[1]Institute of Plasma Physics of NSC KIPT, Kharkov, Ukraine;
[2]National Technical University "Kharkov Polytechnic Institute", Kharkov, Ukraine;
[3]National Technical University of Agriculture, Kharkov, Ukraine;
[4]Project Centre for Nanotechnology and Advanced Engineering, NCSR "Demokritos", Athens, Greece
[a]avtaran@ukr.net, [b]garkusha@ipp.kharkov.ua, [c]vtaran@kipt.kharkov.ua, [d]a.mamalis@inn.demokritos.gr

Zirconium nitride (ZrN) ceramic with cubic structure attracts considerable attention due to its high wear, fatigue and corrosion resistance properties. ZrN coatings are widely used as hard, refractory and bioinert coating in industry and medicine [1-4].

Plasma based PVD coatings have favorable residual stresses, higher density and better adhesion compared to other techniques. It was shown earlier that the utilization of vacuum-arc evaporation with RF discharge allows applying ZrN coatings onto dielectrics and termoliable instrument at low temperature decreasing the amount of macro-particles emitted from plasma flow [5]. The developed technology allowed producing coatings with hardness variation from 26.6 to 31.5 GPa.

The plasma based ion implantation and deposition method (PBII & D) provides the highest adhesion of all currently known PVD deposition methods. According to this technology, the processed object is immersed in the plasma and an impulse negative potential is applied to it. In this case, the product being processed becomes a part of a certain ion source in a more general sense. Here, the ion acceleration occurs in a dynamic self-organizing boundary layer, which is formed around the target surface under a pulsed negative potential. High adhesion is provided due to the formation of a thin transition layer between the substrate and the tool surface [6]. A significant decrease in the temperature of synthesis of coatings to 100-150°C was also achieved due to this method. The effective control of the compressive stresses in the coating during low-temperature synthesis conditions was also achieved due to ion implantation, even at relatively low energies (0.5-5 keV). The internal stresses were found to depend on the amplitude of the pulses and their repetition rate [7].

The nano-crystalline films of zirconium nitride have been synthesized using PBII&D technique on AISI 430 stainless steel at 150°C. Structure examinations – X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) with microanalysis (EDX), nanoidentation method – were performed to study phase and chemical composition, surface morphology, microstructure and nanohardness of coatings. The stressed state was studied by the X-ray tensometry technique (a-$\sin^2\psi$ method) and its modified variants in application to condensates with a strong axial texture.

For ZrN coating application installation "Bulat-6" has undergone a corresponding modernization. For this purpose, a pulse voltage generator with adjustable pulse amplitude, their duration and repetition frequency was developed. ZrN coatings were applied on the surface of stainless steels 20 × 20 × 2 mm (AISI 430). Chemically pure zirconium (99.999) was used as a cathode material. Nitrogen at a purity of 99.999% was used as an active gas. Typical surface morphology of ZrN coating is shown in Fig.1a, b. The surface of the coating is cellular with so-called "honey-comb" type structure with a cell size of 0.5-2 µm (Fig.1a). A possible reason of cells formation is the non-uniform surface sputtering of a growing coating by ions from a gas-metal plasma accelerated by the negative potential of the substrate during the coating deposition. There is low amount of macro-particles with dimensions of about 0.1-5 µm (Fig.1b). According to EDX microanalysis, the relative content of elements in the coating was 5.36 wt% C, 16.60 wt% N, 2.27wt% O and 75.77wt% Zr.

XRD data revealed (111), (222), and (220) main reflections of ZrN phase with a crystal structure of B1 NaCl cubic lattice type (according to JCPDS 35-0753, a = 0.4577 nm lattice constant).The high intensity of the ZrN (111) Bragg peak, indicates that the ZrN grains grow with the [111] preferred orientation perpendicular to the growth plane.The average grain size in accordance with FWHM comprised 13 nm. According to X-ray tensometry data, the crystallites in the condensate are under the action of compression deformation in the film plane and the action of compressive stresses in the system is about 1.94 GPa. The level of microdeformation comprises $\varepsilon \approx 4.85 \cdot 10^{-3}$. The maximal value of nanohardness reached 44 GPa with elastic modulus 500 GPa (Fig.2).

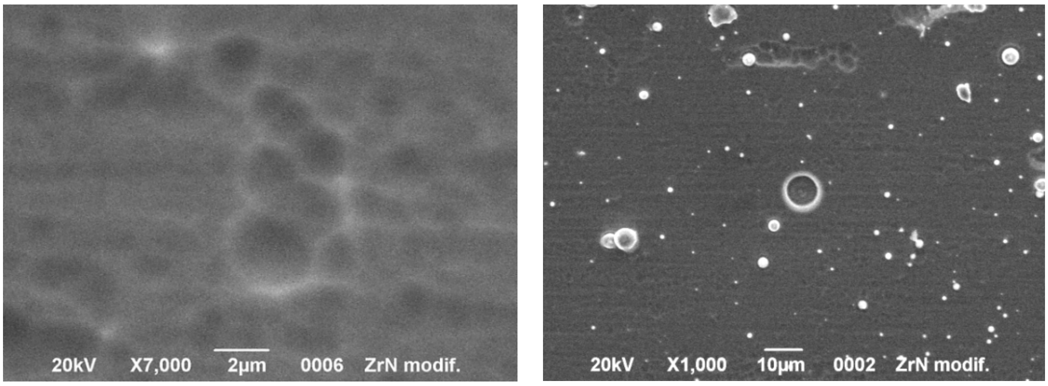

Fig.1. SEM images from ZrN coating on AISI 430 at various magnifications

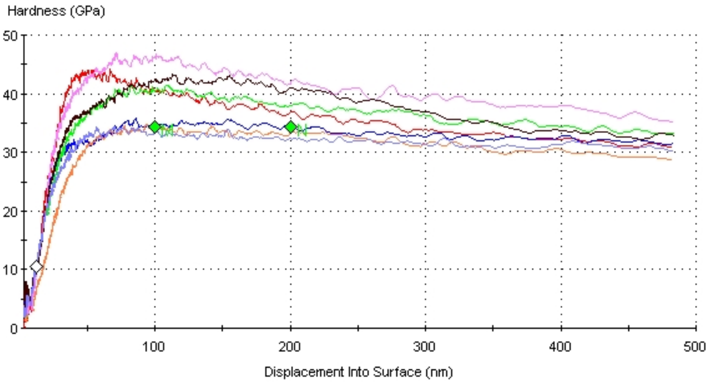

Fig.2. Hardness values in accordance with nanoidentation tests

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