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TRANSITION METAL NITRIDES: FORMATION AND CHARACTERIZATION

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ABSTRACT

Transition metal nitrides- CrN, AlN and ZrN - were deposited by Direct Current Magnetron Sputtering (DCMS) technique. The CrN and AlN films were produced on W320 tool steel with preliminary treatment of electron-beam hardening and plasma nitriding. Their structure, mechanical and tribological characteristics (hardness, elasticity modulus and wear resistance) of the above mentioned coatings were assessed by means of X-Ray Diffraction, Nanoindentation tester and pin-on-disk method.The results exhibit a presence of face centered cubic CrN and hexagonal AlN phases. The hardness values are 19.6 GPa and 15.4 GPa for CrN and AlN layers, respectively. It was found out that the samples with deposited CrN coating possess higher wear resistance compared to one from AlN. Specimens of tool (X12MF) and Chromium-nickel (CrNi 321) steels were utilized at deposition of ZrN coatings. The diffractograms of these films show peaks of ZrN phase. The calculated lattice parameters are in agreement with ICDD (International center for date diffraction) database.

INTRODUCTION

Hard coatings of metal nitrides are now commonly utilized in fields of cutting and forming tools, bearing and machine parts, dies and moulds. They have proven their capability to increase tools lifetime and performance not only during abrasive action of hard materials but also in many chemically aggressive environments [1-3].

Titanium and chromium nitride coatings are gaining popularity in the mechanical manufacturing industry due to their unique properties as high hardness [4], resistance to wear and corrosion [5], chemical and high temperature stability. Besides, they have a promising prospect for applications in biology, medicine, photoelectronic devices and green-energy [6,7].

TiN coating is deposited by magnetron sputtering on Al substrate 7075-T6 [8]. The authors investigated the temperature influence, nitrogen leaking velocity, power on hardness, roughness, adhesion and microstructure of the produced TiN films during the process. Raising of the substrate temperature, reactive gas leaking speed and power leads to higher hardness of the specimens. TiN hardness value is 840 HV while one of the initial material is 170 HV. It is found enhancement with 14% of the surface hardness, 4.1% of adhesion and 9.43% of the surface roughness.

In studies [9-11], the researchers evaluated antimicrobial and antibacterial properties of TiN coatings. The films alloying with Ag increases strongly their ability to remove bacteria from surface them. The layers are obtained by pulse sputtering from two targets – Ti and Ag, as Ag concentrations ranged between 4.6 and 16.7 atomic per cent. It is proved that at Ag concentration to 4.6% is formed solid solution in TiN lattice. On the other hand, the higher concentrations lead to dissolution of Ag ions in the lattice and separation of precipitates in form of nanoparticles with 20-50 nm sizes on TiN polycrystalline grains limitations. Besides, the alloying with Ag enhances significantly antibacterial action and wear resistance independently from the concentration but decreases the hardness. It is shown that higher Ag concentration corresponds to improved antibacterial properties which is prerequisite for application of TiN in medicine and food industry.

The scientists in [12] demonstrated a possibility for coatings deposition from Ti/TiN (different bilayer period) via radio frequency magnetron sputtering on NbFeB substrates with a total thickness of 2.5 μm. The results exhibit better protection against corrosion of Ti/TiN with 6 bilayer period compared to single TiN film. Tribological test is carried out with an artificial saliva and shows enhanced wear resistance of the discussed coatings. The measured hardness is 2.5 times higher than one of the substrates.

CrN films are fabricated on 6959 tool steel by radio frequency magnetron sputtering [13]. The effect of substrate temperature and nitrogen gas flow on adhesive strength and microhardness of the deposited coatings is studied. Higher substrate temperature and lower nitrogen flow rate lead to remarkable improvement in the mechanical properties of the coatings. The best values of the hardness and strength- 736 HV and 28 N- are achieved at a substrate temperature of 400°C and a nitrogen gas flow of 11.58 sccm.

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In work [14], influence of substrate voltage on the structure and mechanical properties of CrN films by DC and pulse magnetron sputtering is assessed. The results show higher nanohardness at increased substrate voltage in case of coatings deposition by pulse magnetron sputtering.

Aluminum nitride (AlN) possesses an excellent combination of properties: high temperature resistance (up to 2200 °C), very good thermal conductivity – 285 W/mK, low coefficient of temperature expansion and good resistance to oxidation (up to 700 °C) [15-17]. These characteristics, as well as the good dielectric and optical properties, makes it a promising candidate for applications in microelectronics, optoelectronics and light industry.

At this stage, the interaction between the structural and emitting properties of multi-cavity pits and super-lattice of AlN (the main components of the high-efficiency emitting diodes and lasers in the blue spectrum) is actively studied. This leads to creation of sources with bright and energy-saving white light [18]. The Al – AlN double layer system is widely used to produce flat panel solar collectors with selectively absorbing coating, as the two-layer vacuum element work in temperature range of -30 °C to +250 °C.

The requirements of enhancement of materials for specific applications have led to the interest in development of newer coating systems. For this reason, the research efforts are directed to study and characterization of coatings from new generation for improvement of mechanical and protective properties of the materials.

The ZrN films have gained much attention lately in different areas of modern industry, such as semiconductors, the diffusion barriers in IC technology, owing to their low resistivity, good corrosion resistance, low formation energy and high mechanical properties [19,20]. Multilayer ZrN/Cu coatings are deposited on 316L stainless steel by reactive DC magnetron sputtering for biomedical applications [21]. The performed investigations show opportunity for enhancement of resistance to corrosion and wear as well bactericidal properties of the metal surfaces.

Other authors [19] investigated the effect of different bias voltage (- 45V, 0V, 50V) on the mechanical properties of ZrN film deposited by DC magnetron sputtering. The results indicate that the introduction of either negative or positive bias results in the degradation of the adhesion properties, while the films under zero bias exhibit the best adhesion. The hardness of the ZrN films increases with raising positive or negative bias, being higher at positive bias.

Using radio frequency magnetron sputtering, in [20] ZrN layers are produced on M2 steel. The XRD results show a presence of ZrN (111) preferred orientation and columnar structure at a power below 300 W. However, the nanohardness enhances and reaches a peak of 34.5 GPa at the same power. At a higher power, the nanohardness decreases significantly to 27.8 GPa. All ZrN films indicate better protection against corrosion than one of the initial material M2.

In the last years, the researchers from a laboratory "Physical technologies" to Institute of Electronics have remarkable achievements in the field of nanotechnologies. One of the field, in which the group worksm is deposition and characterization of nitride and oxide coatings by DC magnetron sputtering. Recent investigations are focusing mainly on preparation and studies of single nitrides (TiN, CrN, AlN, ZrN, VN) and multilayer ones as TiN/WN, TiN/CrN and TiN/ZrN as well oxide as TiO_2, Al_2O_3, CrO_2, Ta_2O_5, TiN/TiO_2. These wear resistant coatings are designed for modern applications such as biomedicine, for optical lenses, selective filters and etc.

The main aim of this study is deposition of nitride coatings by PVD method on different initial materials to evaluate the dependence between structure, mechanical and tribological properties of the obtained films.

In the present work, a possibility for deposition of nitride coatings by reactive DC magnetron sputtering is exhibited. The variation of structure, mechanical and tribological properties of CrN and AlN coatings with technological parameters is investigated. These films are produced on tool steel with preliminary treatment combining electron beam modification and plasma nitriding. Besides, ZrN coatings are formed successfully on various substrates as their phase composition and lattice parameters are studies.

MATERIALS AND METHODS

The experiments were carried out on specimens of W320, X12MF and CrNi (321) steel for deposition of nitride coatings. The first substrate is preliminary processed with electron beam treatment and plasma nitriding.

The electron beam treatment with scanning electron beam was performed on Leybold Heraus (EWS 300/15–60) at the following technological parameters: accelerated voltage – U=55 kV, electron beam current – I=40 mA, speed of the specimen movement – V=4 cm/s, frequency of the electron beam – f=1 kHz.

The plasma nitriding surface treatment was performed on "ION 500" at 600 °C for 8–24 h, in a gas mixture of 70% N2 + 30% H2. After the nitriding process, the samples were cooled down at a high vacuum state in order to minimize the residual stresses and the oxidation.

Transition metal nitrides- CrN, AlN and ZrN - were deposited by Direct Current Magnetron Sputtering (DCMS) technique. The used targets Cr, Al and Zr have a purity of 99.99 %. Before the deposition, the substrate surface was etched by Ar+ plasma for 10 min to remove contaminations and oxide layers from their surface. The CrN and AlN films are obtained on W320 samples in Ar-N2 atmosphere with a working pressure of $1.2x10^{-1}$Pa and $7.5x10^{-2}$ Pa, respectively. The substrates temperatures during the process are 360°C for CrN and 290°C for AlN. ZrN coating is produced on X12MF and CrNi (321) substrates at a working pressure of $1x10^{-1}$Pa and 250 °C.

X-ray diffraction (XRD) experiments were performed on a URD6 Seiferd & Co diffractometer with Cu Kα radiation. The XRD patterns were recorded within the range from 30° to 80° at 2θ scale with a step 0.1°.

Nanoindentation was carried out using Nanomechanical Tester (Bruker). The nanohead of the Nanoindenter performs indentation tests, where the applied load and displacement are continuously monitored, generating load versus displacement data for a test specimen. The Young modulus and hardness are derived from the unload data segments through is situ monitorring of the force vs. displacement plot and automatic calculations by utilizing the Oliver-Pharr method [22,23] are performed. Prior to indentation, the sample surface of the studied composites was polished. The software program prepared for this experiment consisted of 4 lines with 12 indentations each (a total of 48 indentations) and spacing of 80 μm. Each indentation was made with a force of 50 mN.

The wear-resistance of the sample surface is estimated using a device for abrasive wear type „thumb-disk" [24]. The required initial conditions for the assessed surfaces are provided by grinding with sandpaper with different grain size and finally polished with diamond paste. The samples are cleaned with a special solution to neutralize the static electricity. The wear-resistance I is determined as:

$$I = \frac{1}{i} \tag{1}$$

where: Δm is the mass loss in the contact interaction for a certain sliding distance L; ρ is the density of the sample surface layer, S is the contact zone area. The intensity of mass wearing $\boldsymbol{i}$ is dimensionless and is defined as:

$$i = \frac{\Delta m}{\rho . S . L} \tag{2}$$

RESULTS AND DISSCUSIONS

Coatings of CrN and AlN deposited on W320 tool steel

Fig.1 represents XRD pattern of the sample with deposited CrN coatings. All diffractions maximums are indexed. Phase identification was carried out with ICDD Database file PDF #11-0065 for CrN crystal phase. XRD diffractogram shows a presence of face centered cubic (fcc) CrN phase with space group Fm-3m (225) and reflections, corresponding to (111), (200), (220) and (311) crystallographic planes. The lattice parameter was estimated to be a = 0.4185 nm which is in agreement with the value published in Database (0.4140 nm).

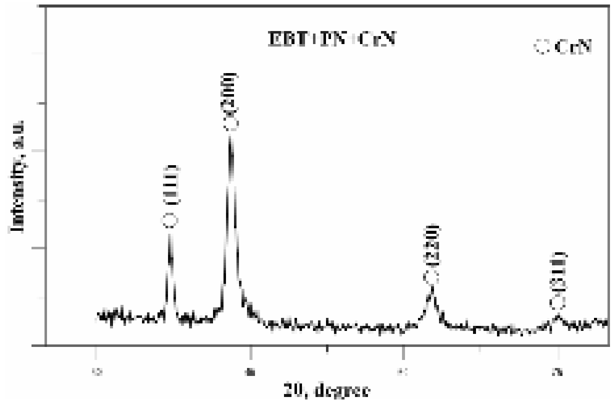

Fig. 1. XRD pattern of the samples with deposited CrN coatings on W320 tool steel

The results from XRD analysis of the sample (W320) with deposited AlN coating are given in Fig. 2. Phase identification was carried out with JCPDS 25-1133 for AlN phase. The diffractogram exhibit peaks of hexagonal (type Wirtzeite) AlN phase with space group p63mc and reflections, corresponding to (100), (002), (102), (110) and (103) crystallographic planes. The measured lattice parameters are a = 0.3111 nm and c = 0.4980 nm, that are close to these ones in the database a = 0.3111 nm and c = 0.4979 (according to JCPDS 25-1133).

Our previous study [25-29] proves that the preliminary treatment with electron beam processing and plasma nitriding lead to improvement of initial materials mechanical properties. Besides, the combination of both methods gives possibility for formation of gradient layers having rough surface and enhanced hardness.

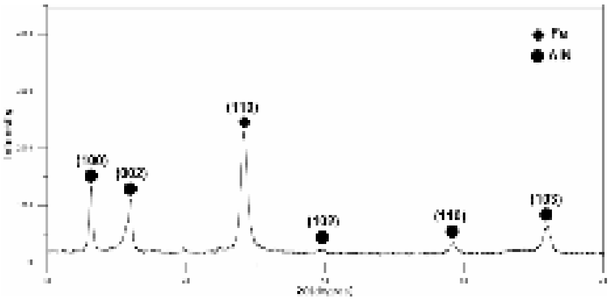

Fig. 2. XRD pattern of the samples with deposited AlN coatings on W320 tool steel

The mechanical properties of the deposited CrN coating were measured by Nanotester and the results are shown in Fig. 3. The average value of the hardness is H=19.649±1.38 GPa and the elasticity modulus achieves a value of E=176.955±10.027 GPa The obtained of us results correspond to published data from other researchers [30-33].

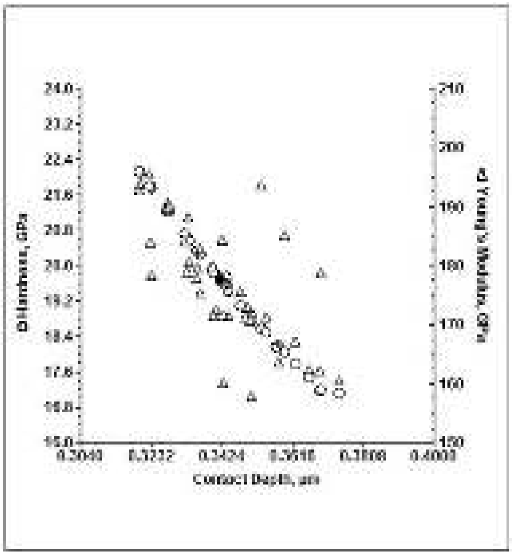

Fig. 3. Hardness and Young's modulus of CrN coatings

Fig. 4 shows results of the measurement of hardness and elastic modulus of AlN coating. The average value of the hardness for AlN coating is H = 15.484±1.472 GPa, evaluated at a contact depth from 0.3 to 0.4 µm. The elastic modulus of AlN coating is E = 170.795±11.367 GPa. The obtained values for the hardness and elastic modulus have good consistency with literature [34-36].

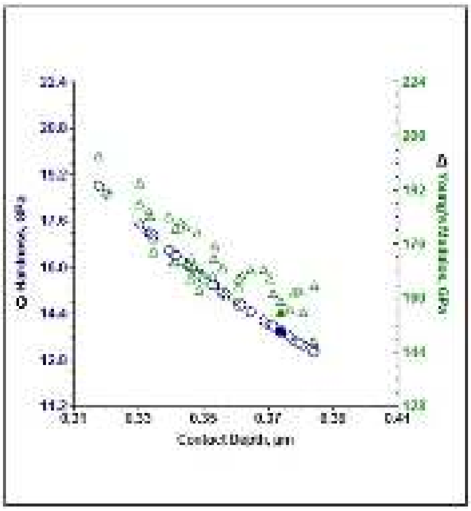

Fig. 4. Hardness and Young's modulus of AlN coatings

Dependence of the wear resistance from the number of cycles for CrN and AlN films is depicted in Fig.5. As it can be seen from the Figure, the wear resistance value diminishes with raising the number of the cycles for both samples. According to the results, the AlN coating owns 5 times higher degree of a protection against wear than the film with CrN.

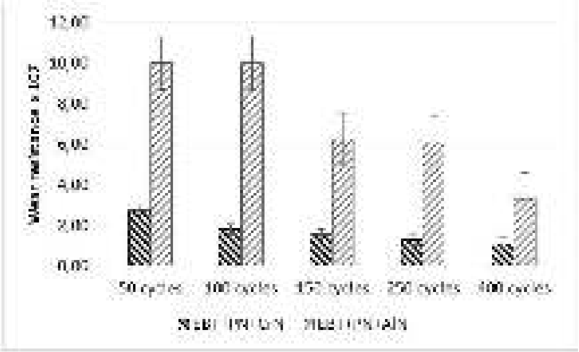

Fig. 5. Diagram of the wear resistance of the specimens at friction path from 50 to 400 cycles

Coating ZrN deposited on tool (X12MF) and Chromium -nickel (CrNi 321) steels

The results from X-Ray diffraction patterns of the ZrN coating, deposited on two types of substrates, are summarized in Fig.6 and Fig.7. The phase of ZrN is observed for both substrates as it has face center cubic structure with space group Fm3m (225). It was found out that the planes correspond to (111), (200) and (311) reflections. For two cases, the lattice parameters are calculated as for X12MF a= 0.4660 nm and for CrNi (321) - a= 0.4658 nm. The obtained results are very close to ones in Database (a= 0.4577 nm).

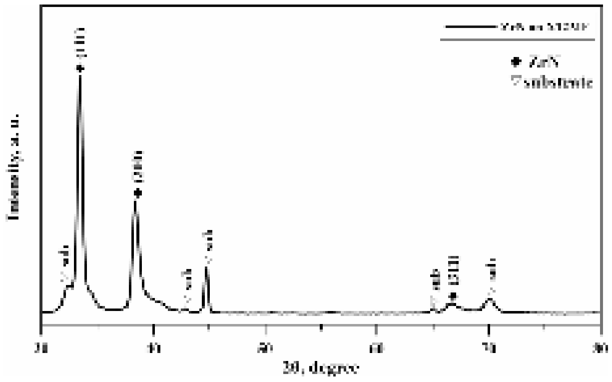

Fig. 6. XRD pattern of the samples with deposited ZrN coatings on X12MF tool steel

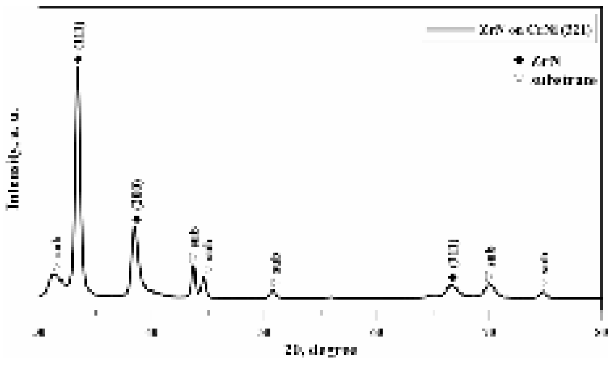

Fig. 7. XRD pattern of the samples with deposited ZrN coatings on CrNi (321) steel

The applied technological conditions during the deposition process give possibility for obtaining of CrN and AlN with lattice parameters close to ones in Database which is an evidence for a small quantity of microstrains in them. On the other hand, these films possess high hardness, elasticity modulus and improved protective properties. Using DC reactive magnetron sputtering, ZrN coating is produced successfully at appropriate parameters of the process.

CONCLUSIONS

Thin ceramic coatings of CrN, AlN and ZrN were fabricated on different metal substrates by reactive DC magnetron sputtering. The preliminary processing of the W320 tool and optimized parameters during the deposition assists for obtaining of CrN and AlN films with good stoichiometry and exploitation properties. The use of various types of substrates for ZrN coating deposition does not influence essentially on the its phase composition.The evaluated lattice parameters of ZrN are an evidence for a presence of a small quantity of microstrains.

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